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U. S. DEPARTMENT OF COMMERCE

BUREAU OF STANDARDS JOURNAL OF RESEARCH

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A METHOD FOR THE STANDARDIZATION OF PERMEAMETERS AT HIGH MAGNETIZING FORCES

By Raymond L. Sanford

ABSTRACT

A description of apparatus suitable for the testing of standard magnetic test bars to be used for the standardization of magnetic permeameters with high magnetizing forces. A criterion is given for determining when accurate values have been obtained. Attention is called to the necessity that the standards shall be magnetically uniform.

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I. INTRODUCTION

With the advent and increasing use of cobalt magnet steels which, on account of their low permeability, require the application of relatively intense fields for magnetization, the question of magnetic testing with high magnetizing forces has come to have considerable practical importance. As the permeameters in general use for commercial magnetic testing have an upper limit of about 300 gilberts per centimeter, it has become necessary to develop methods to apply up to 1,000 gilberts per centimeter or even higher. Several such methods have been devised and are in use in various commercial laboratories. Comparative tests carried out under the auspices of a committee of the American Society for Testing Materials have revealed the fact that the results of measurements on the same sample by different methods generally do not show satisfactory agreement. The data do not show consistent differences between the methods and give no indication of the accuracy attained by any one method. The discrepancies are particularly noticeable in the observed values of coercive force, differences as great as 25 per cent being not uncommon. In view of the fact that considerable quantities of material are purchased on the basis of specifications as to magnetic quality, it is important to know the accuracy of the various commercial testing methods.

In a previous paper,[1] the requirements of bars to be used as magnetic standards for the testing of permeameters were outlined and the Burrows permeameter was recommended for the calibration of magnetic

[1] Sanford, Standards for Testing Magnetic Permeameters, B. S. Jour. Research, 4 (RP140), p. 177; 1930.

standards. As the upper limit of magnetizing force with this apparatus is of the order of 300 gilberts per centimeter, however, it is necessary to adopt some other method for calibration at higher values. An investigation of possible methods of calibrating standard bars at magnetizing forces up to 1,000 gilberts per centimeter was, therefore, undertaken with the end in view of selecting a suitable method for checking the accuracy of commercial permeameters in this range.

II. CHOICE OF A METHOD

The primary consideration in the choice of a standardizing method is accuracy. Furthermore, it should be possible to determine the accuracy attained without reference to measurements by any other method. An additional consideration in the present case is that, in order to determine the effect of size of sample on the accuracy of a given method, it is desirable that the standardizing method should not be restricted to any particular size or shape of specimen.

In any magnetic testing method, the principal condition which must be fulfilled for accurate results is that there shall be no leakage from that part of the bar covered by the test coils. Leakage leads to a nonuniform longitudinal distribution of magnetizing force, and thus produces an error in the observed results. Leakage can be eliminated in the case of a uniform straight specimen by applying the magnetizing force directly to the specimen by means of a magnetizing coil surrounding it and compensating for the reluctance of joints and yokes by means of extra windings over suitable parts of the magnetic circuit.

For magnetizing forces of the order of 1,000 gilberts per centimeter, however, there is some objection to surrounding the specimen with the magnetizing coil on account of heating due to the magnetizing current. It is known [2] that the change in permeability brought about by an increase in temperature of only a few degrees is too great to be neglected in measurements in which an accuracy of 1 per cent is required. Furthermore, in order that the magnetizing current need not be excessive, it is well to include only a comparatively short length of the specimen in the test.

For measurements with relatively intense fields, several methods based upon the well-known isthmus method of Ewing and Low [3] have been devised. In its original form, the method is not suitable for the present purpose because it requires the preparation of samples of a specified size and shape and is not adapted to the determination of points on the hysteresis loop. The modification of this method by Cheney,[4] which is employed at the National Bureau of Standards, is limited to the use of a cylindrical specimen 6 mm. in diameter. The methods of Campbell and Dye [5] and of Webb and Ford [6] are either subject to limitation as to size of sample or apply the magnetizing force by means of a coil surrounding the specimen. It was

[2] Sanford, Temperature Coefficient of Magnetic Permeability Within the Working Range, B. S. Sci. Paper No. 245; Bull. B. S., **12**, p. 1, 1915. Spooner, Temperature Coefficients of Magnetic Permeability of Sheet Steel, Phys. Rev., **27**, p. 183; 1926.

[3] Ewing and Low, Magnetization of Iron in Strong Fields, Proc. Roy. Soc., **42**, p. 200; 1887.

[4] Cheney, Magnetic Testing of Straight Rods in Intense Fields, B. S. Sci. Papers **15** (No. 361), p. 625; 1920.

[5] Campbell and Dye, The Magnetic Testing of Bars of Straight or Curved Form, J. Inst. Elec. Eng., **54**, p. 35; 1915.

[6] Webb and Ford, Precision Permeability Measurements on Straight Bars and Strips in the Region of High Permeability, J. Inst. Elec. Eng., **67**, p. 1302; 1929.

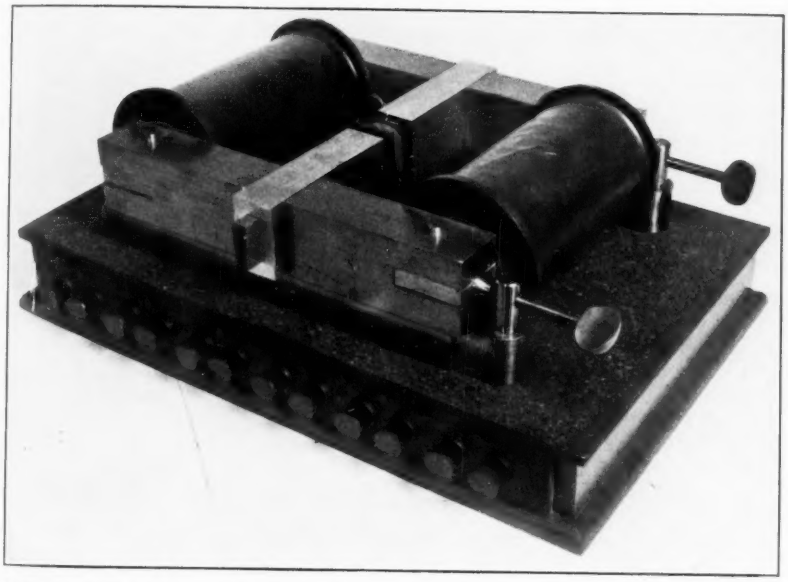

FIGURE 1.—*Apparatus for magnetic measurements with high magnetizing forces*

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decided, therefore, to investigate the possibilities of a slightly different arrangement in which the pole pieces are constructed so as to accommodate specimens of rectangular cross sections. A separate set of pole pieces and test coils is required for each size of specimen to be tested and the specimens must be accurately machined to size. Although this limitation would be serious from the standpoint of routine testing, it is relatively unimportant in standardization work where only a limited number of samples is required. With a method of this type, leakage from the specimen can not be eliminated, but, by proper proportioning of the parts of the magnetic circuit, the error due to leakage can be made negligible for magnetizing forces higher than about 50 gilberts per centimeter.

III. DESCRIPTION OF APPARATUS

Figure 1 shows the apparatus. The specimen is clamped in the symmetrical laminated yoke through pole pieces which serve to provide contact surfaces of large area and to shorten the length of the air gap in which the magnetizing field is measured. Special pole pieces and test coils are made to fit each specimen, which must be accurately ground to dimensions. The design of the pole pieces is indicated in the sketch of Figure 2. They consist of channel pieces of soft iron and filler strips of the same material, of such dimensions that when the specimen is inserted, there is a thickness of 1 cm at each side of the specimen. The filler strips are slightly over 1 cm thick so that they can be firmly clamped against the specimen when inserted in the yoke. Since the specimens are accurately ground to size, they are not strained by clamping, and this effect may be neglected. The separation between the pole pieces can be adjusted at will. The magnetomotive force is provided by means of magnetizing windings mounted on the yokes.

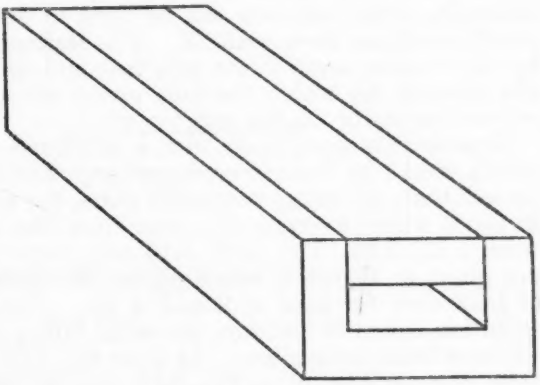

FIGURE 2.—*Pole pieces*

The test-coil system is wound on a split brass form having bakelite flanges. There are five test coils in all, 1 cm long and wound with 100 turns each. The first coil is wound directly on the form, insulated from the brass by a layer of thin paper. The second coil is separated from the first by a uniform layer of paper so that there is an annular space between them, and so on. With this arrangement, it is possible by connecting successive coils in series, opposing, to measure the field at four different distances from the specimen and thus by extrapolation to determine the field at the surface. This, according to theory, is equal to the magnetizing force acting on the specimen.

For making the measurements, the usual battery, rheostats, reversing and selector switches, and resistance coils for sensitivity adjustment are used and need not be described in detail. The galvanometer is Leeds & Northrup ballistic instrument having a free period of 24 seconds and an external resistance for critical damping of approximately 20,000 ohms. The instrument is of sufficiently high sensitivity so that it can be used with a parallel resistance as low as 200 ohms to give heavy overdamping, thus minimizing errors due to relatively slow flux change in the specimen. For calibration, a standard mutual inductance is used, the calibrating current being measured by a Brooks deflection potentiometer and standard shunts.

IV. OBSERVATIONS AND RESULTS

As stated above, it is not possible to eliminate leakage from a specimen not surrounded by a magnetizing coil, but the effect can be minimized so as to be negligible in measurements with magnetizing forces exceeding about 50 gilberts per centimeter. It remains to determine what criterion can be used to determine that the proper conditions have been realized. The leakage conditions are affected by the relative areas of the pole face and specimen cross section and the distance by which the pole pieces are separated, which will be referred to simply as the gap.

Experiments were made with a specimen of hardened 36 per cent cobalt steel 1 by 3 cm in cross section. The test coils were so proportioned that, by using successive pairs, the field could be determined in zones whose average distances from the surface of the specimen were 1.35, 3.30, 5.35, and 7.10 mm, respectively. Typical results are given in Figure 3, which shows the distribution at three values of induction for gaps of 2 and 3 cm. For the 3 cm gap the distribution is nearly uniform, the value falling off only slightly with the distance from the surface. At 2 cm the field increases with distance from the surface up to the 5.35 mm distance and then falls off. Extrapolation leads to the same value at the surface for either value of the gap. It is probable that, for a gap intermediate between the two, the radial distribution would be practically uniform as far as the test coils extend. The value of gap for uniform distribution will vary with the size of the specimen and the area of the pole pieces.

Although these results seemed to indicate that the correct value of magnetizing force had been obtained, there was some question whether there might not be a sharp drop in the field between the first zone and the surface due to the joint between the pole pieces and the specimen. In order to check this point, experiments were made with special cobalt-steel specimens prepared with great skill by the research department of the Westinghouse Electric & Manufacturing Co. These specimens were 23 cm long with a section 2.50 by 1.85 cm. A hole approximately 9 mm in diameter was drilled longitudinally along the axis of each specimen. Even though they were drilled before the specimens were heat treated, the holes remained remarkably straight.

Pole pieces and test coils were made to fit the drilled specimens, and another test coil 1 cm long was wound on a cylindrical form which would just fit in the hole. By means of this inner test coil the field within the specimen could be determined. Measurements were made with gaps of 3, 4, and 5 cm. The values at 4 and 5 cm gave concordant

results, and the extrapolated values agreed with those determined by means of the inner test coil as shown in Figure 4. For the 3 cm gap, however, the extrapolated values did not agree with those obtained with the inner coil. The extrapolated values were higher and the inner-coil values were lower than for the longer gaps at the same induction. The reason for this is evident from the curves of Figure 5 which show the longitudinal distribution of H within the specimen for the different values of gap. If the pole pieces are too near together, leakage from the specimen to the pole-piece faces leads to a nonuniform longitudinal distribution of both B and H over the length of the specimen covered by the test coils.

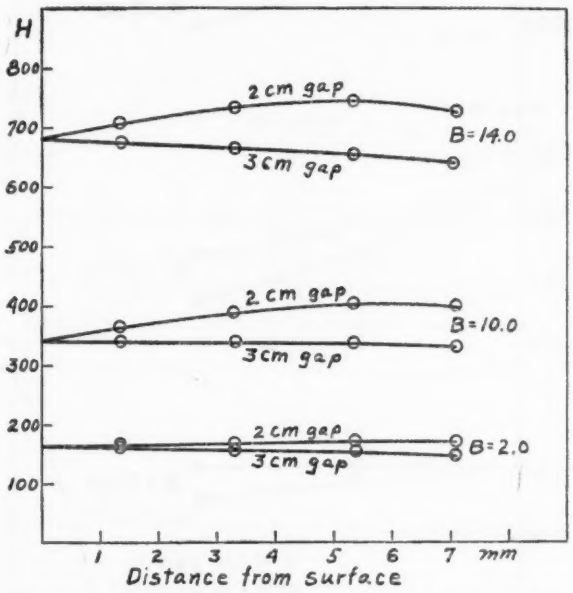

FIGURE 3.—*Radial distribution of H for 1 by 3 cm specimen*

Magnetizing force, H, in gilberts per centimeter. Induction, B, in kilogausses

These results would seem to indicate that if the extrapolated values obtained with two or more gap distances are in agreement, this can be taken as a criterion that the leakage from the part of the specimen covered by the test coils is not excessive. The results thus obtained are estimated to be accurate within 1 per cent.

V. MAGNETIC STANDARDS

In an earlier paper,[7] the writer has called attention to the importance of the degree of uniformity in bars which are to be used as magnetic standards. The effect of nonuniformity is most pronounced in the second stage of magnetization, where the slope of the normal induction curve is greatest, and is usually negligible in the third stage where the slope is smaller. At first thought, it might appear that this factor would be of even less importance where measurements are to be

[7] Sanford, Standards for Testing Magnetic Permeameters, B. S. Jour. Research, 4 (RP140), p. 177; 1930.

made with relatively intense magnetizing forces. As a matter of fact, the production of bars of cobalt magnet steel sufficiently uniform to be satisfactory for use as magnetic standards has proved to be the most difficult part of the problem. The curves shown in Figure 6 are

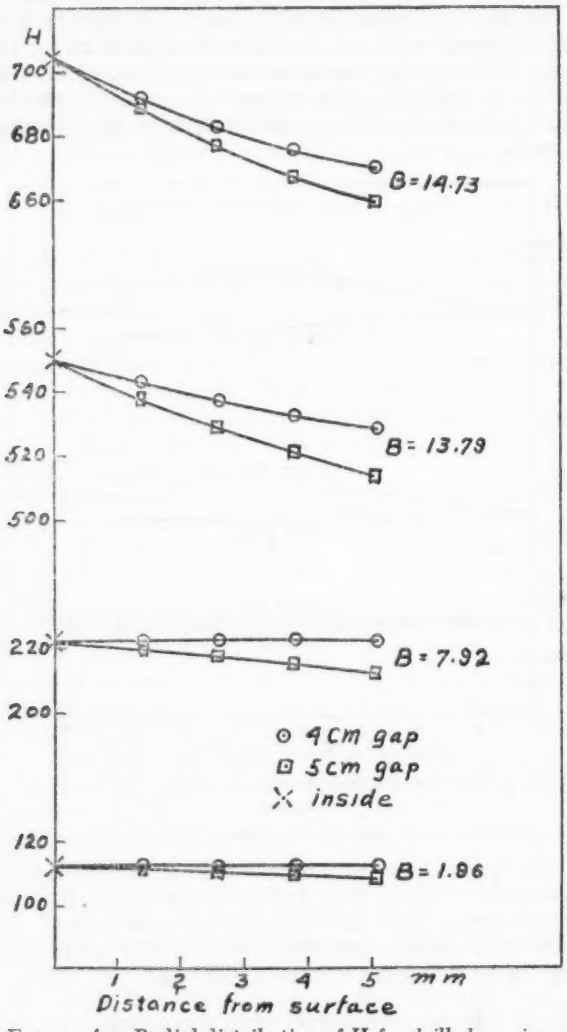

FIGURE 4.—*Radial distribution of H for drilled specimen*

Magnetizing force, H, in gilberts per centimeter. Induction, B, in kilogausses

typical of the conditions commonly found. The bar on which the observations were taken is magnetically soft at one end, the most conspicuous difference being observed in the coercive force, which varies in value from 60 to 160 gilberts per centimeter. It is obviously not fair to judge the accuracy of a method involving from 12 to 20 cm of the length of such a bar by the results obtained with another

method involving only 1 cm of the bar, no matter how accurate the second method may be. It is probable that lack of uniformity is responsible in large part for the differences observed when identical

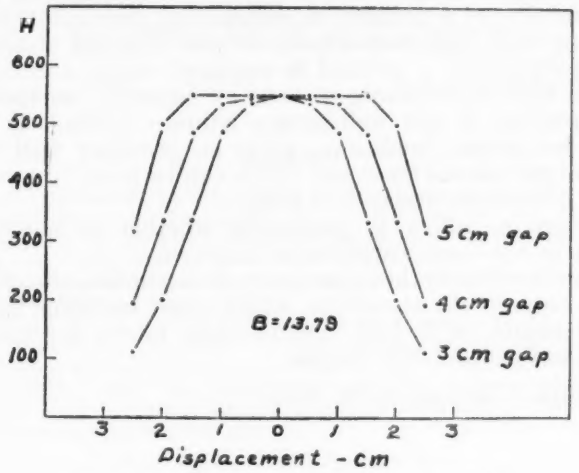

FIGURE 5.—*Longitudinal distribution of H*

Magnetizing force, H, in gilberts per centimeter. Induction, B, in kilogausses

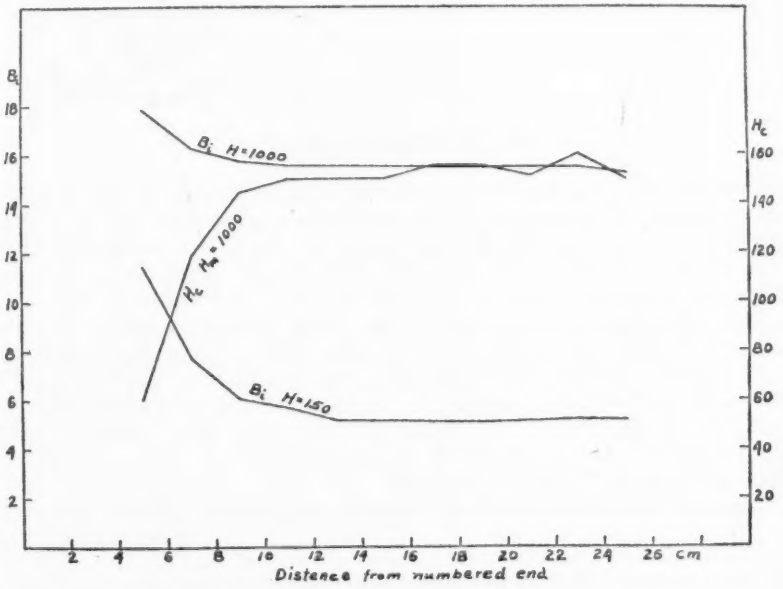

FIGURE 6.—*Degree of uniformity of bar C–930*

Intrinsic induction, B_i, in kilogausses. Coercive force, H_c, in gilberts per centimeter

bars are measured by different methods. It is still necessary, therefore, to take into account the uniformity of the bars to be used as magnetic standards even for measurements with high magnetizing forces.

VI. SUMMARY

The advent and increasing use of cobalt magnet steels requiring the application of relatively intense fields for magnetization has led to the development of a number of commercial permeameters for magnetic testing with high magnetizing forces. For the standardization of these instruments a method is required whose accuracy can be determined without reference to tests by any other method.

An adaptation of the well-known isthmus method is described, which, under proper conditions, gives an accuracy well within the allowable experimental error and which can be made to accommodate specimens of various shapes and sizes.

A criterion by which to determine whether or not the proper conditions for accuracy are obtained is given.

Attention is called to the importance of magnetic uniformity in bars to be used as magnetic standards, which must be taken into account in measurements with high magnetizing forces no less than in measurements in the lower ranges.

WASHINGTON, December 30, 1930.

DETERMINATION OF THE TOLUENE CONTENT OF A MIDCONTINENT PETROLEUM [1]

By Johannes H. Bruun,[2] R. T. Leslie,[2] and Sylvester T. Schicktanz[2]

ABSTRACT

Commercial petroleum fractions from an Oklahoma crude oil were subjected to an extensive fractional distillation culminating in a set of 1° cuts. Toluene was found in all of the cuts boiling within the range 90° to 112° C. The amount in each cut was determined by nitrating it quantitatively to 2, 4-dinitrotoluene by means of a nitrating procedure which was found not to attack any of the other constituents of the fractions.

Practically all of the toluene was found in the fractions boiling below 110° C. the boiling point of pure toluene. The largest fraction, boiling between 98° and 99° C. contained the larger amount of toluene, but the maximum concentration of toluene (32 per cent) was found in the fraction boiling between 107° and 108° C. The total amount of toluene found corresponded to one-third of 1 per cent based upon the crude petroleum.

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I. INTRODUCTION

A variety of methods have been proposed and used for the determination of the aromatic hydrocarbons (as a group) in various petroleum fractions, and a few attempts have been made to determine the amount of an individual hydrocarbon of this class in a given crude oil. Schorlemmer [3] was one of the first to prove the presence of toluene in a Pennsylvania crude oil. Mabery,[4] in his pioneer work on American petroleum, estimated that an Ohio petroleum contained about 0.03 per cent of toluene. Mabery and Hudson [5] found 54 per cent of toluene in the fraction of a California petroleum which distilled between 109° and 110° C. Most of the toluene in this crude oil was found in the fractions which distilled near the normal boiling point of pure toluene (110° C). However, Young,[6] in working with a Pennsylvania oil, noticed that most of the toluene distilled far below its own boiling point.

[1] This paper describes some of the results obtained in an investigation on The Separation, Identification, and Determination of the Chemical Constituents of Commercial Petroleum Fractions, listed as project No. 6 of the American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by John D. Rockefeller. This fund is being administered by the institute with the cooperation of the Central Petroleum Committee of the National Research Council.

[2] American Petroleum Institute research associate.

[3] C. Schorlemmer, Lieb. Ann., **127,** p. 311; 1863.

[4] C. F. Mabery, Proc. Am. Acad., **31,** p. 34; 1894.

[5] C. F. Mabery and E. I. Hudson, Proc. Am. Acad., **36,** p. 259; 1901.

[6] S. Young, J. Chem. Soc., **73,** p. 918; 1898.

The amount of toluene in petroleum fractions has usually been determined by treatment with a mixture of nitric and sulphuric acids, the decrease in volume after this treatment being used as a direct measure of toluene. This method is also used for the determination of aromatic hydrocarbons as a group in petroleum fractions and has been described by Egloff and Morrell [7] and by Faragher, Morrell, and Levine.[8]

In the investigations on an Oklahoma petroleum four of the isomers of hexane [9] as well as *n*-octane [10] have previously been isolated. The present paper, which is a continuation of these investigations, describes the detection of toluene in the same oil and its removal and determination by means of nitration.

II. METHODS EMPLOYED

The lower boiling fractions of an Oklahoma petroleum were first fractionated by distillation into 1° cuts. Preliminary nitration tests indicated that toluene was present in all fractions boiling between 90° and 112° C. The absence of other nitratable aromatic constituents, such as benzene and xylenes in these particular fractions, was proved by comparing the melting points of the preliminary nitro products with the melting point of pure 2, 4-dinitrotoluene. It was also proved by the absence of nitratable material in the fractions boiling immediately above and below those containing the toluene. The presence of benzene and of xylenes in other fractions will be discussed in a later paper.

The absence of unsaturated compounds was demonstrated by means of the iodine numbers which were found for the fractions before nitration.

The toluene was then removed from the fractions by treatment with the following nitrating mixture:

10 volumes H_2SO_4, 66° Bé. (specific gravity 1.84).
2 volumes H_2SO_4, fuming (23 per cent free SO_3).
15 volumes HNO_3, fuming (specific gravity 1.49 to 1.50).

By the use of this concentrated acid at low temperatures it was found possible to convert practically all of the toluene into 2, 4-dinitrotoluene without any appreciable amount of mononitro products (or trinitrotoluenes).

Before nitration the hydrocarbons were cooled to about 5° C. The nitrating acid was added dropwise while rapidly agitating the mixture, which was maintained at all times below 10° C. When all the acid had been added, a rapid agitation was continued for 30 to 60 minutes. The hydrocarbon layer was separated in a separatory funnel, after which the acid layer containing the dinitrotoluene was poured into a beaker containing crushed ice and agitated for half an hour. The dinitrotoluene was then filtered, washed with water, and dried. A small amount of dinitrotoluene mixed with mononitrotoluene remained in solution in the hydrocarbon layer. This amount was recovered by subsequent distillation. Traces of mononitrotoluene, which were obtained in this way, were converted into the dinitrotoluene by

[7] G. Egloff and J. C. Morrell, Ind. Eng. Chem., **18**, p. 354; 1926.
[8] W. F. Faragher, J. C. Morrell, and I. M. Levine, Ind. Eng. Chem., Anal. Ed., **2**, p. 18; 1930; and the references there cited.
[9] J. H. Bruun and M. M. Hicks-Bruun, B. S. Jour. Research, **5**, pp. 933-42; 1930.
[10] R. T. Leslie and S. T. Schicktanz, B. S. Jour. Research, **6**, p. 377; 1931.

further nitration. From the weight of the dinitrotoluene the amount of toluene was then calculated.

The melting point of each nitro-product was determined. Owing to the presence of small amounts of occluded monitrotoluene and unnitrated hydrocarbons, the melting point was in some cases a few degrees below 70° C. (the melting point of pure dinitrotoluene), but by crystallization from alcohol the melting point could in every case be raised to 70° C.

A blank run on an unnitrated toluene-free fraction indicated that the nitrating treatment did not remove or attack the aliphatic or the naphthenic hydrocarbons.

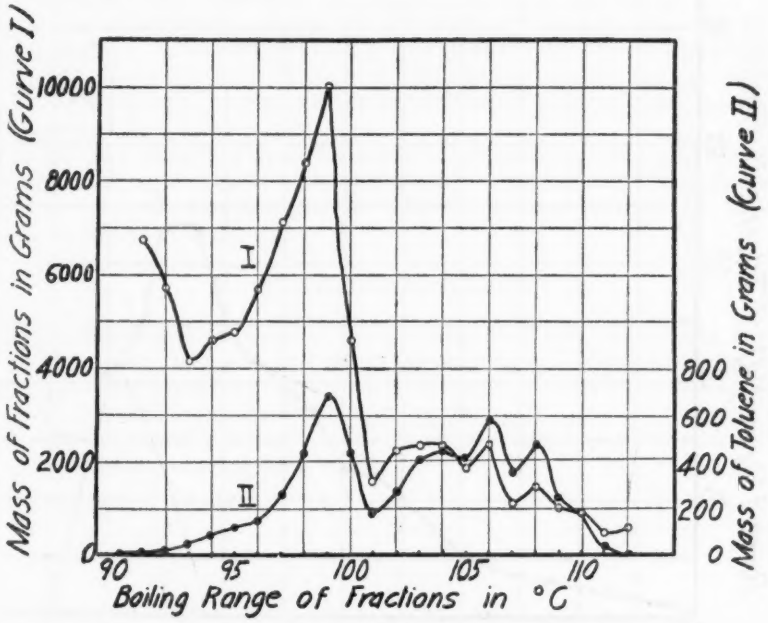

FIGURE 1.—*Distribution of the distillates (Curve I) and of the toluene (Curve II) after extensive fractional distillation*

Curve I shows the weight of fraction (left ordinate scale) plotted against boiling range. Curve II shows the weight of toluene in fraction (right ordinate scale) plotted against boiling range of fraction. Each point on the curve indicates the end point of a given cut.

Another test was carried out with petroleum ether free from aromatic and olefine hydrocarbons. Two grams of toluene were added to 200 ml of the petroleum ether. During the subsequent nitration no petroleum ether was lost and the toluene was quantitatively recovered as dinitrotoluene.

III. EXPERIMENTAL PROCEDURE

1. DISTILLATION

The material used was of the lower boiling fractions from 600 gallons of crude oil,[11] which had been distilled in a semicommercial still

[11] The crude was obtained from No. 6 Well of South Ponca Field, Kay County, Okla. See Washburn, Bruun, and Hicks, Bur. of Stds. J. of Res., 2, p. 469, Table I; 1929.

in an oil refinery.[12] Three hundred to four hundred liters of this material was first fractionated in a laboratory rectifying still[13] with 20 bubbling cap plates[14] of steel. The fractions from the laboratory still having boiling point ranges from 70° to 130° C. were subjected to extensive fractional distillation in smaller bubbling cap stills[10 14] of Pyrex laboratory glass. These distillations were carried out at a rate of about 1 ml per minute and with a reflux ratio of about 10 : 1. A fraction was taken for every 1° increase in the temperature of distillation. In this way 60 different fractions were obtained between the

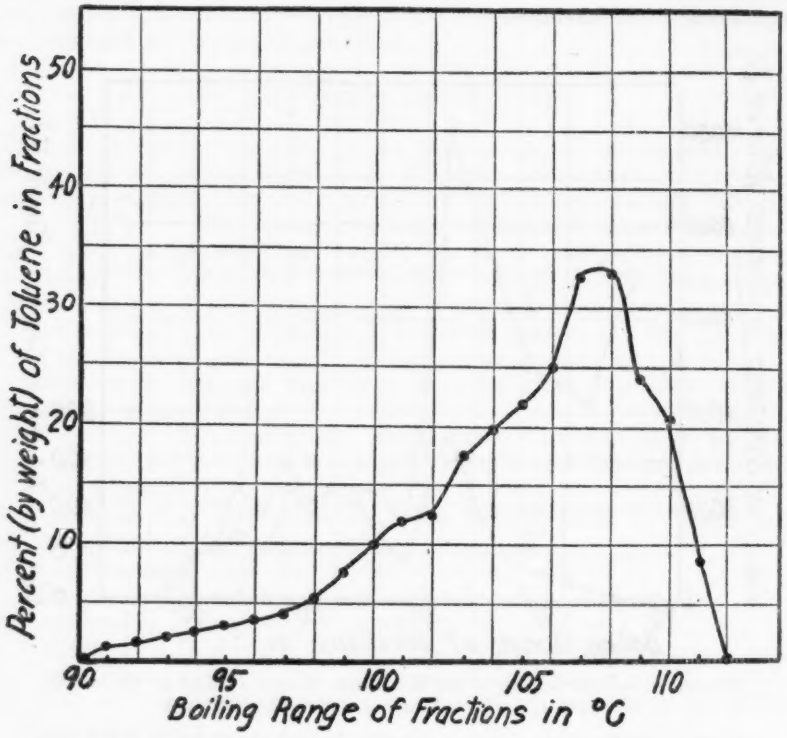

FIGURE 2.—*Percentage of distribution of toluene in fractions after extensive fractional distillation*

Ordinate: Percentage of toluene in fraction. Abscissa: Boiling range of fraction.

temperatures 70° and 130° C. Toluene was found in 22 of the fractions which had distilled within the range 90° to 112° C. and was removed by nitration.

2. NITRATION

Each of the fractions boiling within the range 90° and 112° C. was nitrated according to the method described. The result of the nitration is shown in Figures 1 and 2.

[10] R. F. Leslie, and S. T. Schicktanz, B. S. Jour. Research, **6**, p. 377; 1931.
[13] Acknowledgment for this distillation is made to A. E. Pew, Jr., and R. B. Davidson of the Sun Oil Company.
[13] E. W. Washburn, J. H. Bruun, and M. M. Hicks, Bur. of Stds. J. of Res., **2**, pp. 470-3; 1929.
[14] J. H. Bruun, Ind. Eng. Chem., Anal. Ed., **1**, p. 212; 1929.

IV. DISCUSSION OF RESULTS

Curve 1 in Figure 1 shows the distribution of the distillates over the boiling range. The largest 1° cut is that boiling between 98° and 99° C. Curve 2 in Figure 1, representing the distribution of the toluene in the different fractions, shows that the large fraction boiling between 98° and 99° C. contained a larger amount of toluene (683 g) than any of the others.

The percentage of toluene by weight in the fractions is represented by the graph in Figure 2, which shows that the maximum concentration (32.2 per cent) of toluene is present in the fraction boiling between 107° and 108° C. This is in accordance with the statement made by Young that the toluene in petroleum fractions distills below its own boiling point. This can probably be explained by the existence of a constant boiling mixture of toluene with other constituents of petroleum. The search for these other constituents is in progress and will be described in a later paper.

A total of 11,589 g of dinitrotoluene equivalent to 5,858 g of toluene was obtained as a result of the nitration. Based upon 600 gallons of crude petroleum (specific gravity 0.9) the toluene content is found to be one-third of 1 per cent.

V. ACKNOWLEDGMENT

The authors wish to express their thanks to E. W. Washburn, chief of the chemistry division, Bureau of Standards, and director of American Petroleum Institute Research Project No. 6, under whose direction this investigation has been carried out.

The authors are indebted to H. A. Barron for assistance rendered in the laboratory during this work.

WASHINGTON, December 20, 1930.

THE MECHANISM OF THE ATOMIZATION OF LIQUIDS

By R. A. Castleman, jr.

ABSTRACT

A discussion is given of the general problem and of some applications of the phenomena of liquid atomization, with especial reference to fuel preparation in internal combustion engines. It is pointed out that both "air" and "solid" injection seem to have physical backgrounds quite similar to that of air stream atomization, and the discussion is limited to the latter.

Some previous work which seems to bear either directly or indirectly on this problem is reviewed, and it is assumed that a necessary step in atomization is the tearing of ligaments from the unatomized mass, these ligaments being of such sizes that they will eventually break up into drops of the sizes observed in the spray.

Brief discussions are given of the applicability of Rayleigh's work on the rate of collapse of liquid columns to the collapse of these ligaments, and of what values of the $\frac{\text{length}}{\text{diameter}}$ ratio and of the degree of instability may be expected to be effective. It is then shown how the sizes of the ligaments can be determined from those of the drops in the spray. Finally, combining (*a*) measurements of the sizes of drops, (*b*) geometrical and physical considerations, and (*c*) Rayleigh's work, it is shown that these ligaments will collapse so quickly at sufficiently high air speed—that is, when true "atomization" sets in—that the droplets will then appear to be picked directly from the main mass, as has been observed.

Certain other observations are shown to be in qualitative agreement with this theory.

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I. INTRODUCTION

The problem of liquid atomization is of interest and importance in the study of internal combustion engines because the great majority of such engines at present do, and probably for some time in the future will, derive their energy from a liquid fuel; which fuel must be supplied under time and temperature conditions not suitable for complete vaporization. While complete vaporization may have occurred in old slow-speed carburetor engines, using the highly volatile

gasoline formerly available, it does not occur in modern high-speed engines of this type, which must use gasoline of much lower volatility. The problem seems even more acute with engines of the Diesel type, in which a fuel of very low volatility is injected directly into the cylinder just before ignition.

This phenomenon is also in other important commercial and technical use (for example, the manufacture of evaporated milk, metal spraying, etc.). It is, in general, employed when it is desired to put a mass of liquid into the finest possible state of subdivision under conditions not suitable for complete vaporization. So far, progress (particularly automotive) has demanded that industry shall not pause for explanation of the mechanism of atomization, but merely investigate the circumstances favoring its production, so that one may supply these and thus obtain the phenomenon. To utilize such processes to the best advantage, however, it is necessary to understand the mechanical background. The problem is evidently of a physical nature; indeed, the very use of the phenomenon in design work—the knowledge that it is only necessary to supply certain physical conditions in order to be sure of obtaining the phenomenon—is tacit acknowledgment of the existence of a definite physical background.

The object of this paper is to put in enlarged and more tangible form a theory of this mechanism advanced in a letter to the editor of the Physical Review.[1] This theory involved two assumptions: (1) That ligament formation is a necessary step between the large mass of liquid and the discrete droplets; (2) that Rayleigh's analysis of the rate of collapse of liquid columns applies, without modification, to these ligaments.

As this work is primarily concerned with the preparation of fuel for combustion in internal-combustion engines, this theory, to be satisfactory, should cover cases found useful for this purpose. There appear to be two of these: (1) Air-stream atomization. In this process air at high speed is passed over the surface of the liquid to be atomized. It is found that, when the relative air speed is sufficiently high, the liquid is broken up into minute drops. This process is outstanding in commercial importance at the present time (gasoline carburetor). High-pressure air injection is a special case of air-stream atomization. (2) "Solid" or "airless" injection. It is found that when liquid is forced under very high pressure (300 to 600 atmospheres) into still air it is finely atomized. (This method was invented years ago, but finds its maximum application to the modern small or high-speed Diesel.) As the high-injection pressure merely gives a high initial velocity to the injected liquid, we see that this case also is similar to air-stream atomization: the fast-moving liquid loses ligaments to the still air in the same way that the fast-moving air drags ligaments from the quiescent liquid.

Since, then, both forms of fuel atomization appear to be physically similar, this analysis will be limited to air-stream atomization. The following symbols will be used:

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[1] Castleman, Phys. Rev., 35, p. 1014; 1930.

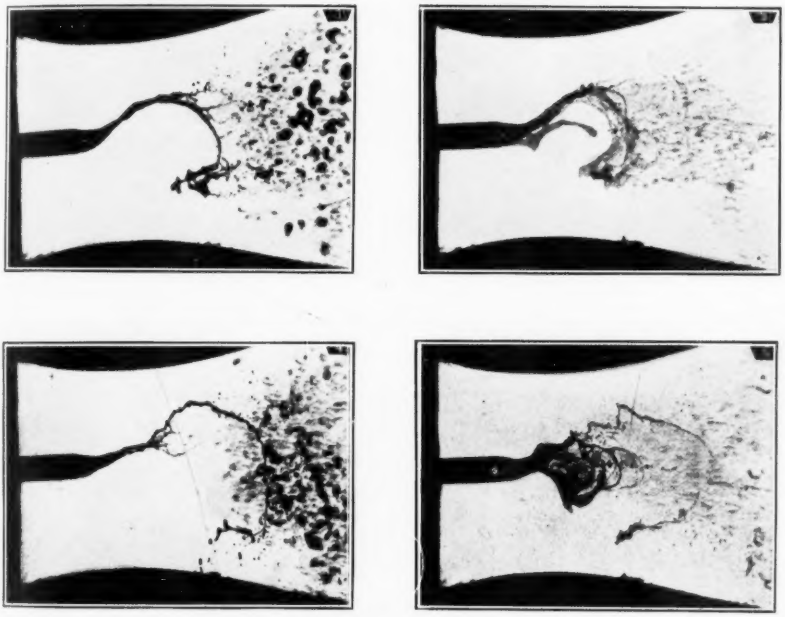

FIGURE 1.—*Atomization of water in model of carburetor throat (Scheubel). Air speed about 2,700 cm/sec.*

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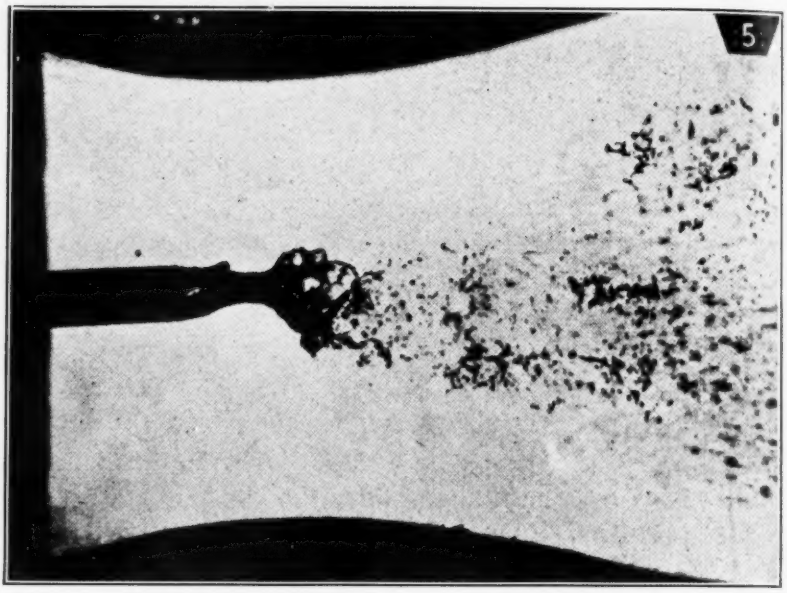


FIGURE 2.—*Atomization of water in model of carburetor throat (Scheubel). Air speed about 5,300 cm/sec.*

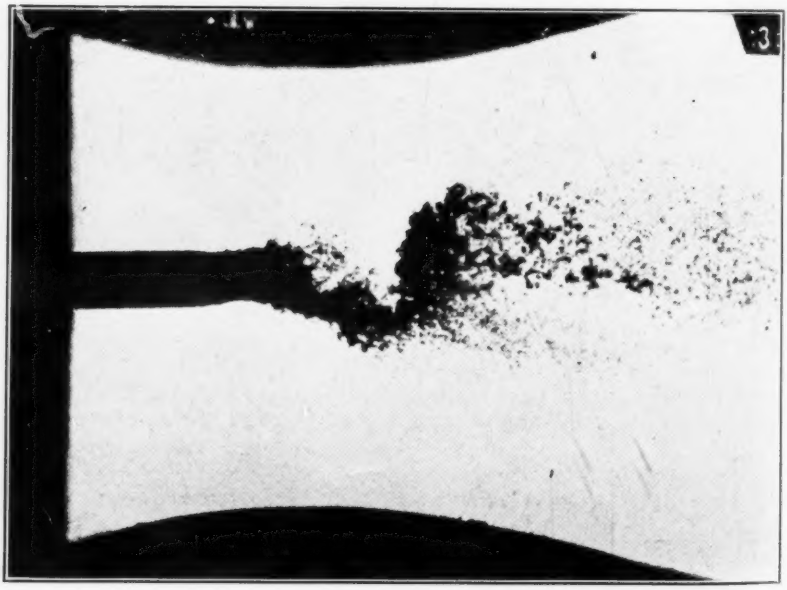


FIGURE 3.—*Atomization of water in model of carburetor throat (Scheubel). Air speed about 10,500 cm/sec.*

TABLE 1

Symbol	Quantity
S	Air speed.
r	Radius of drop.
R	Radius of ligament.
L	Length of ligament.
Z	Ratio $\frac{L}{2R}$.
σ	Density of liquid.
T	Surface tension of liquid.
a	Amplitude of surface disturbance.
t	Time.

II. PREVIOUS WORK

1. DIRECTLY BEARING ON ATOMIZATION IN AN AIR STREAM

(a) DROP SIZE

Sauter,[2] measuring photometrically the mean size of the drops formed when water is atomized in an air stream, found that this varies with the air speed, thus: At low air speeds the mean radius r is relatively large. As the air speed is increased r rapidly decreases, finally asymtotically becoming about 6 μ at an air speed (at the point where the liquid is introduced) of 10,000 to 12,000 cm/sec. Remembering that Sauter's definition of the mean size gives more prominence to the larger drops and that others have shown that the degree of inhomogeneity of the spray decreases with increase in air speed, it seems that we may take $r=5$ μ as a conservative estimate for drop size of water atomized in a high-speed air stream.

(b) MECHANISM OF ATOMIZATION

F. N. Scheubel [3] has obtained some interesting and instructive spark pictures of the process as it occurs in the carburetor throat. He atomized both water and alcohol in an air stream. Figure 1[4] shows some of his results with water at a low air speed of about 2,700 cm/sec. The ligaments torn off are clearly visible. Figure 2 was taken at a higher air speed, about 5,300 cm/sec. The ligaments, while still visible, appear both finer and shorter. In Figure 3, taken at the comparatively high air speed of 10,500 cm/sec., the ligaments have largely vanished, and the small drops appear to be torn directly from the main mass. This, it may be assumed, happens at all higher air speeds.

While Scheubel's work constitutes an excellent description of the process of atomization in an air stream, his interpretation of the results, by dimensional analysis, throws little light on the intermediate physical processes.

2. THE COLLAPSE OF A LIQUID COLUMN

Plateau [5] showed that a round cylindrical liquid column whose length exceeds its circumference is unstable and will, therefore, even-

[2] J. Sauter, Forschungsarbeiten auf dem Gebiete des Ingenieurwesens, No. 312; 1928.
[3] F. N. Scheubel, Wissenschaftliche Gesellschaft für Luftfahrt (WGL), p. 140; Jahrbuch, 1927.
[4] Figures 1, 2, and 3 were copied from Scheubel's article in the 1927 W. G. L. Jahrbuch. The scale of reproduction of Figures 2 and 3 is about 50 per cent greater than that of Figure 1.
[5] J. A. F. Plateau, "Statique expérimentale et théorique, etc."; Paris, 1873. (Cited by Rayleigh.)

tually collapse under the influence of any disturbance, even one of arbitrarily small amplitude. He was not concerned with the time required for the collapse to take place. As disturbances are always present, any long column of liquid, such as a jet, will eventually break; but, as the disturbances vary greatly, both in initial size and in rate of growth, such a collapse is ordinarily a very irregular affair.

This collapse can, however, be made so beautifully regular that it may readily be viewed by stroboscopic means, if the chamber from which the jet issues be influenced by a periodic vibration of proper amplitude and frequency. Pictures, taken by the writer, showing such phenomenon in a falling jet of water, are shown in Figure 4. Figure 4 (*a*) is a spark picture, while Figure 4 (*b*) was taken through a stroboscopic disk, which allowed an exposure frequency equal to that of the disturbance (in both these cases a tuning fork produced the disturbance). It is to be noticed that the amplitude is, for some time, of hardly perceptible depth, then it grows rapidly until it equals the jet's radius, when the jet breaks. Such a manner of growth suggests that it is of the exponential type.

Lord Rayleigh seems to have been the first to recognize clearly the practical importance of the rate of collapse, and, therefore, of certain geometrical and physical properties of the column influencing its dynamic behavior. In his analysis of this effect [6] an infinitely long cylinder of liquid at rest and initially in equilibrium under the influence of the tension of its envelope was assumed, and the relative upsetting efficiency of disturbances cutting off various lengths of the surface of this cylinder was investigated. For this purpose the change in potential energy from that prevailing in the equilibrium configuration was computed from geometrical considerations; while that portion of the kinetic energy that arises from the deformation of the column was determined on the assumption that the velocity of growth of α could be derived from a potential. Application of Lagrange's method then gave the time rate of variation of α; and this equation was solved on assuming a relation of the form:

$$\alpha = \alpha_o \cdot e^{qt} \tag{1}$$

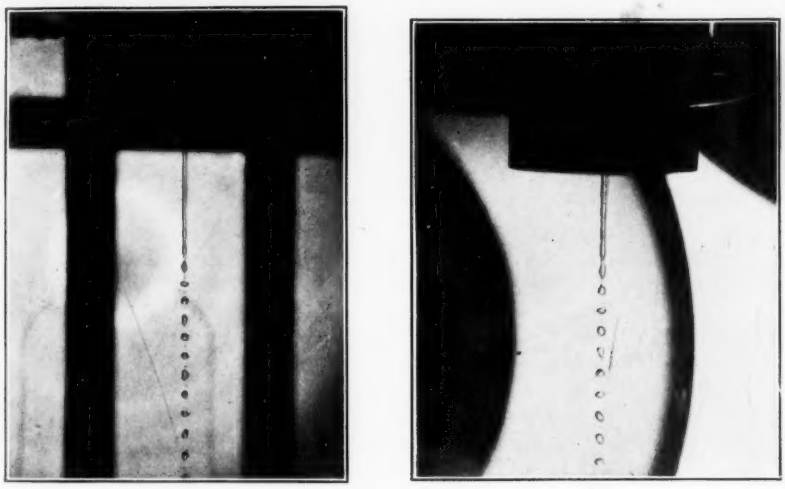
where α_o is the initial value of α. It followed that

$$q = \left(\frac{T}{\sigma R^3}\right)^{1/2} \cdot F \tag{2}$$

where F is a (dimensionless) function of Z only.

Rayleigh pointed out that the disturbance which results in the largest value of q will preponderate if the time of collapse is long enough; therefore, as he was primarily interested in comparatively coarse and slowly collapsing jets, it seemed sufficient to determine the maximum value of F. In many other cases, however, particularly the present one, the argument does not seem so simple, and it has seemed desirable to put Rayleigh's results in a form better adapted to the general case. This has been done by the writer,[7] and some values of F are thus shown in Figure 5.

[6] Rayleigh, Proc. Lond. Math. Soc., **10**, 4; 1879. (Sci. Papers, art. 58); Theory of Sound, Chap. XX.
[7] Castleman, Nature (Lond.) **114**, p. 857; 1924.



a *b*

FIGURE 4.—*The collapse of a round jet falling in still air*

a, Spark pictures; *b*, stroboscopic picture.

III. MECHANISM OF ATOMIZATION

1. GENERAL

What we wish to explain is, how a stream of air at high speed can tear small drops directly from the main mass of liquid, so that the liquid appears to explode into droplets. The procedure that will be followed is indicated in Scheubel's pictures, though this theory was virtually worked out before these pictures were noticed.[8] We assume that a necessary step in atomization is the tearing of ligaments from the unatomized mass, these ligaments being of such sizes that they will break up into drops of the sizes observed in the spray; and we shall examine whether these ligaments will collapse quickly enough to give the appearance observed, the appearance of drops being torn directly from the main mass of liquid (if the life of a ligament does not exceed about 10^{-4} sec., the appearance, when allowance is made for lag of the drops behind the air stream, would be similar to that shown in fig. 3.)

2. THEORY

(a) APPLICABILITY OF RAYLEIGH'S ANALYSIS

It is first necessary to consider whether Rayleigh's analysis, which was made for a different purpose, is applicable to this case. Four questions seem pertinent: (1) How far may we expect that these ligaments correspond to the cylindrical segments considered by Rayleigh? (2) Are conditions favorable for the existence of a velocity potential? (3) What extraneous forces may be expected to act and what should be their effect? (4) Is the contained volume sensibly constant during the collapse?

1. Rayleigh, it appears, was considering the case of at least two consecutive surface disturbances. Without going deeply into the matter, however, it appears that this same treatment should also apply to the growth of a single surface distrurbance in a cylinder already closed at one end. Hence, it should cover the present case.

2. For a velocity potential to exist, both rotation and viscosity must exert negligible influence on the motion. Little can be said of the former, except that there can be no consistent rotation before the ligament starts to be drawn from the main mass; hence, the only chance it will get to grow to harmful proportions is before the length of the ligament grows equal to its circumference, since the ligament collapses too soon after this. As to the viscosity effect, the mean radial velocity, even in extreme cases, would seem to be too small for the viscosity to seriously affect the result.

3. The only external force is the friction of the air. How much effect this can have depends largely on the ligament's life period, which will appear to be very brief.

4. In the case considered the ligaments are so fine and consequently collapse so quickly that it seems improbable that a volume change of amount large enough to affect these conclusions can occur during this time.

[8] It was, in fact, remarked some nine years ago by W. S. James, when a member of the staff of this bureau (J. Soc. Auto. Eng., 8, p. 549; 1921), that those interested in atomization problems would find "very suggestive reading in the article on Capillary Action, by Lord Rayleigh in the 11th ed. of the Encyclopedia Britannica."

(b) MEAN SIZE OF LIGAMENTS

As it seems impossible to make direct measurements of ligament size when atomization sets in, it is necessary to determine the relation between ligament size and drop size. Since a ligament of radius R and length $Z \cdot 2R$ becomes a drop of radius r, we have:

$$2ZR \cdot \pi R^2 = \frac{4}{3}\pi r^3$$

$$R = \left(\frac{2}{3Z}\right)^{1/3} \cdot r \tag{3}$$

so that, by equation (2), for the same final value of r

$$\frac{q_1}{q_2} = \frac{F_1(Z_1)^{1/2}}{F_2(Z_2)^{1/2}} \tag{2-a}$$

We shall limit our attention for the present to the maximum value of F, which is 0.343 and occurs at $Z = 4.5$. In this case $R = 0.53\ r$.

(c) THE LIFE PERIOD OF A LIGAMENT

Taking for r the value we deduced from Sauter's work, 5×10^{-4} cm, we have 2.65×10^{-4} cm for R, so that $q = 6.8 \times 10^5$ sec.$^{-1}$ for water at 20° C. Putting equation (1) in the form:

$$t = \frac{1}{q} \cdot ln\,(\alpha/\alpha_o) \tag{1a}$$

and noting that this ligament breaks when α grows to 2.65×10^{-4} cm, while α_o can not be much less than 10^{-8} cm, since the molecular diameter is around 10^{-7} cm, we have for an upper limit to the collapse time $t = 1.5 \times 10^{-5}$ sec. (If we take for α_o the more probable value of 10^{-5} cm, t will be only about one-third as great.) Thus the ligament life period, computed from Sauter's observations of drop size for water, assuming this to have been at around 20° C., and using the maximum value of F, corresponding to $Z = 4.5$, appears to be brief enough to account for such phenomena as are recorded in Figure 3.

(d) EFFECTIVE VALUE OF Z

As the above computations were based on the maximum value of F, it is necessary to inquire whether, and in how far, other cases need be considered. This we shall do by comparing, for a series of values of Z, the life periods of the corresponding ligaments, each starting with the same value of α_o and leading to the same final value [9] of r (5×10^{-4} cm). Remembering that α must grow to R for rupture to to occur, we obtain from equations (1a), (2a), and (3)

$$\frac{t_Z}{t_{4.5}} = \frac{q_{4.5}}{q_Z} \cdot \frac{ln\,\frac{R_Z}{\alpha_o}}{ln\,\frac{R_{4.5}}{\alpha_o}} = \frac{0.055}{F_Z(Z)^{1/2}}\,(13.9 - \log_{10} Z) \tag{5a}$$

[9] As this argument is based on observed values of r it seems proper to consider one value of r at a time, although a given sample of spray contains drops having quite a variety of these values.

for $\alpha_o = 10^{-3}$ cm; and

$$\frac{t_Z}{t_{4.5}} = \frac{0.170}{F(Z)^{1/2}} (4.92 - \log_{10} Z) \qquad (5b)$$

for $\alpha_o = 10^{-5}$ cm.

From these equations, and data from Figure 5, we obtain Table 2.

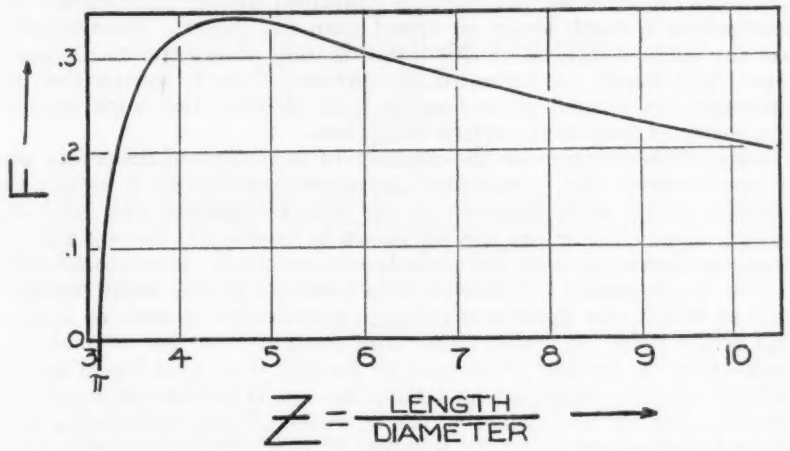


FIGURE 5.—*Dependence of degree of instability of a round liquid column upon ratio—* $\frac{length}{diameter}$

TABLE 2

Z	F	$t_z/t_{4.5}$	
		$\alpha_o = 10^{-3}$cm	$\alpha_o = 10^{-5}$cm
3.20	0.100	4.14	4.18
3.30	.180	2.23	2.28
3.50	.270	1.45	1.48
4.00	.325	1.13	1.13
4.50	.343	1.00	1.00
5.00	.338	.96	.95
7.00	.280	.97	.93
9.00	.230	1.03	.97

In words (remembering that Z increases from an initial value of zero, since the ligament is torn directly from the unatomized mass), it appears that a quicker disruption will result for $Z = 4.5$ than for any smaller value. As we have seen that this will result in a life period brief enough to account for observed phenomena, it follows that no larger values need be considered, and that we may take $F = 0.343$ at $Z = 4.5$ as the effective values.

3. COMPARISON WITH OBSERVATIONS

We have seen that, on the basis of Rayleigh's work and Sauter's drop-size observations, the kind of atomization described by Scheubel is to be expected. There remains to compare, on the basis of the present theory, some more observations by Sauter and by Scheubel, apparently independent of this theory and of each other.

Scheubel's pictures show that the ligaments vary much in size and length at the same air speed. On the above theory this agrees with Sauter's observations that there is a marked variety of drop sizes at a given air speed; for this implies a corresponding variety in the sizes and a much greater variety in the rates of collapse of the ligaments.

Scheubel also found that alcohol exhibited similar phenomena, but atomized at a much lower air speed than did water. Remembering that the surface tension of this liquid is only about one-third that of water, this result, in terms of the present theory, means that the ligaments are formed more readily with alcohol, the work required for a given extension of surface being less.

Sauter's observation of the manner of variation of drop size with air speed—that the mean size decreases rapidly to a practically constant value with increase in air speed—accords well with the present theory. For, as the air speed is increased, the sizes of the ligaments decrease, their life periods become much shorter, and much smaller drops result. However, this decrease in size soon reaches a limit at which the ligaments collapse practically as soon as formed. This is the point at which true "atomization" (in the etymological sense—that no smaller drops can be formed from this liquid by this method) may be regarded as setting in. It is further interesting to note that Sauter and Scheubel are in virtual,[10] and apparently independent, agreement as to the location of this point; for Sauter found that his curve of size of drop *v.* speed of air flattened at about 10,000 to 12,000 cm/sec., while Figure 3 of this paper indicates that Scheubel has not quite reached complete atomization at a mean air speed of 10,500 cm/sec.

IV. CONCLUSION

The actual process of atomization in an air stream seems rather simple: A portion of the large mass is caught up (say, at a point where its surface is ruffled) by the air stream and, being anchored at the other end, is drawn out into a fine ligament. This ligament is quickly cut off by the rapid growth of a dent in its surface, and the detached mass, being quite small, is swiftly drawn up into a spherical drop. (A quite similar phenomenon occurs when a large drop is detached from a tube. The chief difference is that the ligament connecting the small drop to the main mass is much finer than that connecting the large drop to the liquid in the tube, and, hence, the time of detachment is enormously less.) The higher the air speed, the finer the ligaments, the shorter their lives, and the smaller the drops formed, within the limits discussed above. The writer's aim has been to show how Rayleigh's work, done over 50 years ago apparently for an entirely different purpose, covers the more modern problem of atomization in an air stream.

Constructive criticism by Dr. N. E. Dorsey proved particularly helpful in the preparation of this paper.

WASHINGTON, December 27, 1930.

[10] Sauter gave the volume of air flowing and the size of the carburetor throat, from which data the air speed in the throat was estimated. Scheubel gave the mean speed directly. In both cases, however, the carburetor would introduce peculiarities in the velocity distribution (see fig. 1) so that finer estimates on this point do not seem justified.

SEPARATION OF NORMAL OCTANE FROM PETROLEUM BY DISTILLATION AND CRYSTALLIZATION [1]

By R. T. Leslie and Sylvester T. Schicktanz

ABSTRACT

An interlocking process of distillation and crystallization is outlined for the separation of *n*-octane from petroleum. The laboratory stills used and various forms of laboratory apparatus suitable for crystallization at low temperatures are described. The boiling point, freezing point, refractive index, and molecular weight of the product are given and are compared with the properties of a carefully purified sample of synthetic *n*-octane. It is estimated that the *n*-octane content of the oil under consideration is not less than 1.0 per cent.

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I. INTRODUCTION

A complex mixture, such as petroleum, in which many compounds with nearly the same boiling point probably exist and in which constant boiling mixtures may be formed, can not be separated into its constituent hydrocarbons by fractional distillation alone.[2] [3] It has been previously pointed out that fractional crystallization might offer a method of breaking up such constant boiling mixtures,[4] [5] [6] but the method has not been very extensively employed in cases in which temperatures much below those attainable with ice mixtures are required. The advent of "dry ice" (solid CO_2) as an article of commerce has extended the usefulness of the method to much lower temperatures.

In addition to the low temperatures necessary, there are other difficulties associated with the general application of fractional crystallization to the problem of separating hydrocarbons. Many of these systems have a tendency to supercool and become highly viscous, especially if their freezing points are very low. Frequently the hydrocarbons cool to vitreous solids even when in a comparatively

[1] This paper describes some of the results obtained in an investigation on The Separation, Identification, and Determination of the Chemical Constituents of Commercial Petroleum Fractions, listed as project No. 6 of the American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by John D. Rockefeller. This fund is being administered by the institute with the cooperation of the Central Petroleum Committee of the National Research Council.

[2] Brooks, Nonbenzenoid Hydrocarbons, Chemical Catalogue Co., pp. 18, 24; 1922.
[3] Young, Fractional Distillation, Macmillan Co., p. 255; 1903.
[4] Young, Fractional Distillation, Macmillan Co., p. 142; 1903.
[5] Washburn, Bruun, and Hicks, B. S. Jour. of Research, **2**, p. 467; 1929.
[6] Sunier and Rosenblum, Ind. Eng. Chem., Anal. ed., **2**, p. 109; 1930.

pure state.[7] The data in the literature on the freezing points of these hydrocarbons are somewhat incomplete apparently for this reason.

In a complex mixture, such as petroleum, it is impossible to predict what may occur on freezing. It is probable, however, that the hydrocarbons will crystallize as solid solutions or eutectic mixtures rather than as molecular compounds if the viscosity does not interfere with normal freezing.[8] If a solid solution results, separation by fractional crystallization will usually be slow. If eutectic freezing occurs in a mixture which is richer in one constituent than the eutectic composition, a single substance may separate first and can then be removed in a pure state except for adhering mother liquid. To be amenable to fractionation by crystallization, therefore, a system of hydrocarbons should not have the eutectic composition.

II. METHOD AND APPARATUS

1. PRELIMINARY DISTILLATION

The material employed in this investigation was a 200-liter fraction of petroleum boiling roughly between 100° and 130° C. which had been obtained by the distillation in a semicommercial still of 2,300 liters (600 gallons) of crude petroleum from well No. 6 of the South Ponca field of Oklahoma,[9] and which was given a further distillation through a metal bubbling-cap column having 20 plates.[10] The 2° to 3° cuts resulting from these distillations were then distilled in 1° cuts in a battery of glass column stills. Each column consisted of 10 to 12 units of the type shown in Figure 1, with a head of the design shown in the same figure, by means of which very high reflux ratios could be obtained. These distillations were continued until considerable separation of the constituents began to occur, as indicated by the distribution of the volumes over the range of boiling points. (See fig. 2.)

After three such distillations further separation became slow, and fractional crystallization was begun on those fractions which gave promise of yielding crystals before they became very viscous. This appeared to be the case only for the fractions in the neighborhood of the boiling point of *n*-octane. The change in the initial freezing point of the cuts with their boiling points is shown in Figure 3. It was found possible to remove material having the properties of *n*-octane from fractions boiling as low as 121° to 122° and as high as 127° to 128°, but below 123° to 124° and above 126° to 127° the process was slow because of the low concentration of *n*-octane, the low temperature required to freeze the fractions, and the high viscosity of the liquid.

2. APPARATUS FOR CRYSTALLIZATION

In designing apparatus for the crystallization, some of the requirements to be met were: (1) Ease in attaining a wide range of low temperatures, (2) ability to cool large quantities rapidly, (3) rapid filtration of viscous material, (4) close approach to equilibrium be-

[7] Kanolt, B. S. Sci. Paper No. 520, p. 625; 1926.
[8] See footnote 6, p. 377.
[9] See Washburn, Bruun, and Hicks, B. S. Jour. of Research, **2**, p. 469; 1929.
[10] Described in B. S. Jour. of Research, **2**, p. 470; 1929.

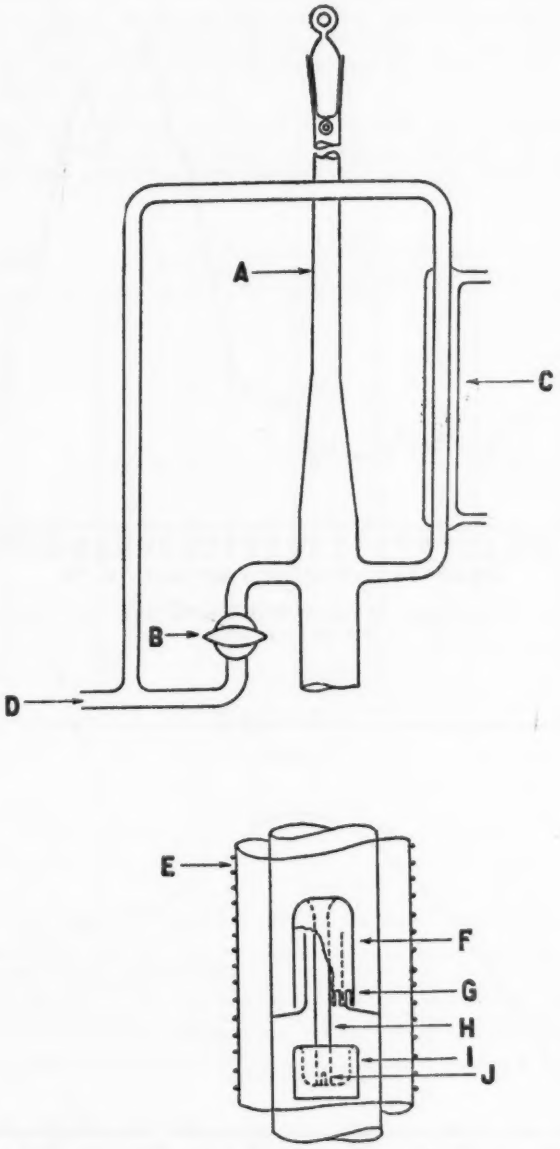


FIGURE 1.—*Essential parts of glass bubbling-cap stills and reflux heads*

A, thermometer well; *B*, stopcock for removing variable portions of condensible gas; *C*, condenser for returning remainder of condensible gas to still head; *D*, exit to condensing system; *E*, glass jacket wound with chromel heating wire; *F*, cap under which vapor passes; *G*, slots ground in cap for breaking up vapor stream into small bubbles; *H*, overflow tube returning liquid to plate below; *I*, cup forming liquid seal to prevent passage of vapor up overflow tube; *J*, slots allowing passage of liquid from tube to cup.

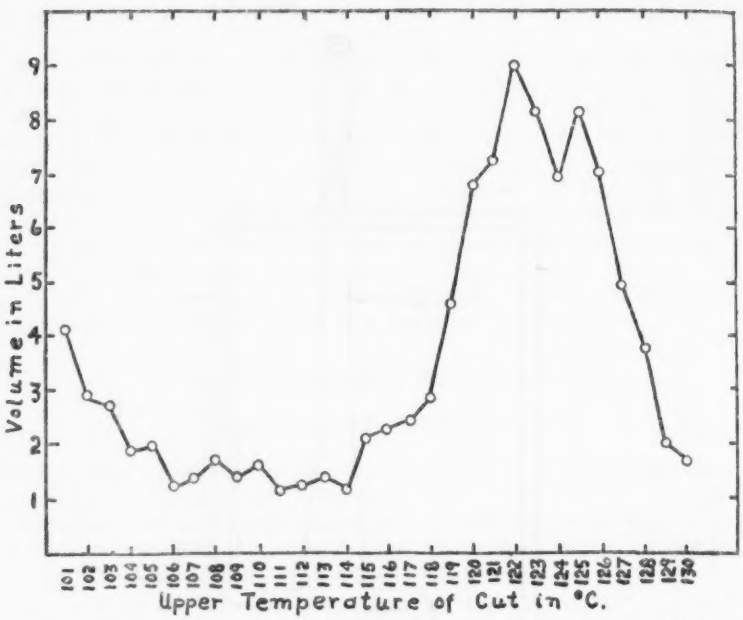


FIGURE 2.—*Distribution of volume with boiling point after three distillations in glass stills*

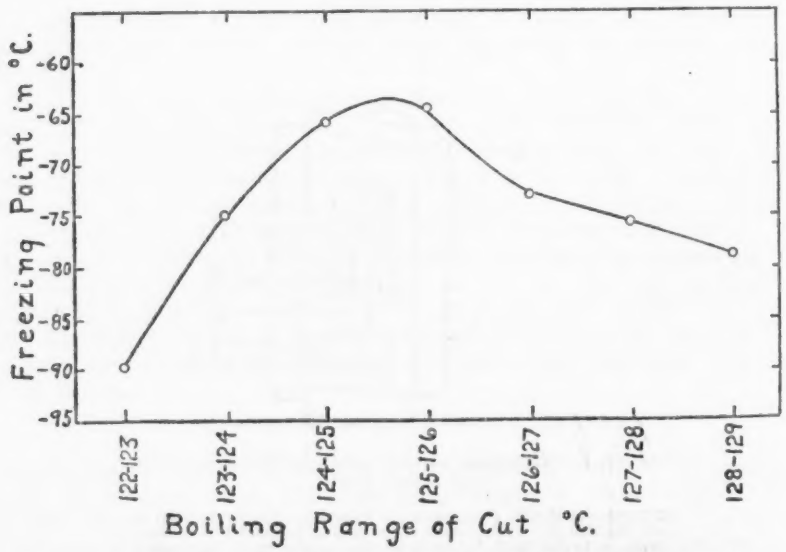


FIGURE 3.—*Change in the freezing point with the boiling point of fractions*

tween phases, and (5) as complete separation of the liquid from the crystals as possible. Several methods for accomplishing these results were tried. In all of them the material was frozen to a slush which was not too thick to permit vigorous stirring so that intimate contact between the phases could be maintained in spite of the low thermal conductivity of the material.

The simplest method consisted in cooling the material in a metal cylinder by means of a slush of carbon dioxide in a mixture of chloroform and carbon tetrachloride till a solid phase appeared and

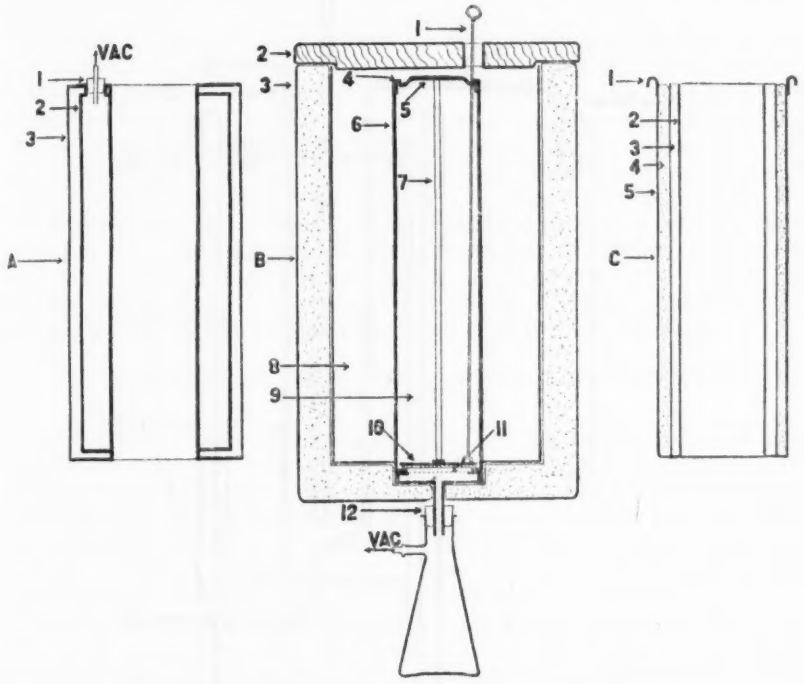


FIGURE 4.—*Apparatus used for fractional crystallization*

A, (1) opening for filling inner chamber; (2) chamber containing carbon dioxide ice in ether; and (3) air space for thermal insulation between inner and outer baths

B, (1) brass rod for withdrawing plate which covers filter surface; (2) wooden cover; (3) felt insulating material (4) brass cleats; (5) phosphor-bronze spring; (6) brass cylinder; (7) rod transmitting pressure from spring to plate; (8) space for freezing mixture; (9) space for mixture to be crystallized; (10) heavy brass disk faced with leather forming liquid-tight seal; (11) copper gauze filter (200 mesh); and (12) rubber stopper.

C, (1) handles; (2) tube fitting snugly over *B-6*; (3) space for cooling or warming agent; (4) felt insulation; and (5) sheet metal

drawing off the liquid with a pipette having a wire gauze tip as filter medium. The cylinder was then withdrawn from the slush and allowed to warm, while stirring, until another fraction could be removed, etc.

A somewhat more effective type of apparatus is shown in Figure 4. The material placed in the central tube of *B* was cooled by carbon dioxide slush in the space surrounding it. In order to reach temperatures somewhat below those attainable by carbon dioxide ice at atmospheric pressure, the drum, *A*, was slipped over the central tube of *B* after preliminary cooling in the usual way, and the pressure was

reduced on the mixture of ether and carbon dioxide ice in *A–2*. As an additional method of varying the temperature, *A* could be replaced by *C*, into the inner annular space of which liquid air could be introduced for further cooling, or a warm liquid if a higher temperature was desired. When the sample had been cooled till a thick

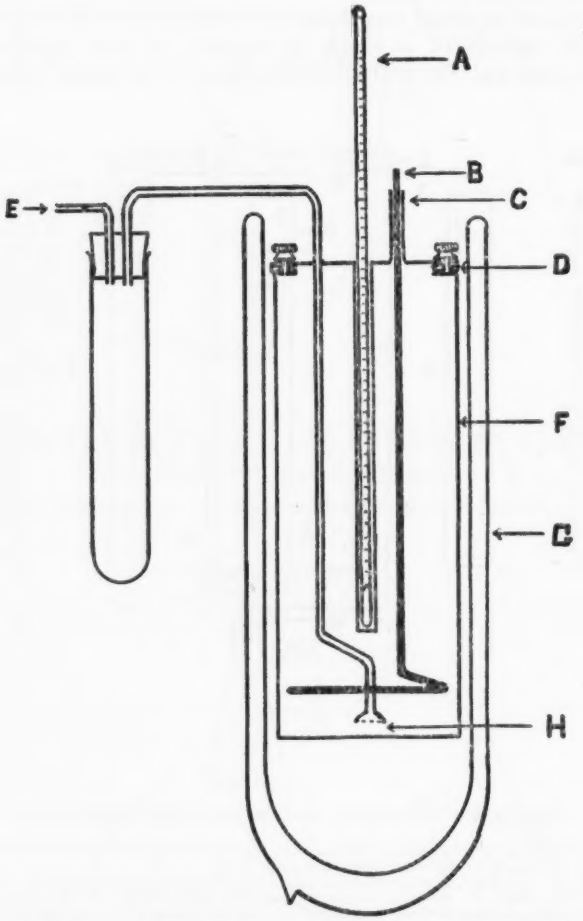


FIGURE 5.—*Apparatus for filtration of viscous materials under pressure*

A, pentane thermometer; *B*, brass rod stirrer; *C*, inlet for compressed gas between stirrer and walls of tube; *D*, leather gasket; *E*, tube to vacuum line; *F*, heavy wall brass cylinder; *G*, Dewar tube; *H*, filter medium

slush resulted, the plate, *B–10*, was removed and the liquid drawn off through the filter gauze.

The best results were obtained with an apparatus of the type shown in Figure 5. The contents of the cylinder were cooled by immersion first in the carbon dioxide slush and then in a Dewar tube containing a small quantity of liquid air. The liquid was forced

through the filter by compressed air entering at C and suction applied at E.[11]

3. METHOD OF FRACTIONAL CRYSTALLIZATION

The fractions of a single distillation which were found to yield octane were each crystallized once separately. This was done because, though a number of fractions could be made to yield octane, some were much richer than others. The resulting fractions were then united for further fractionation, since their indices of refraction and freezing points were approximately the same; and the mother liquors were redistilled or combined on the basis of their refractive indices.

In order to remove the octane as completely as possible, it was necessary to perform a systematic fractionation. Two slightly different procedures were employed, in one of which equilibrium melting was allowed to continue with each lot frozen until the final crystals were sufficiently pure to be considered as product. This method resulted in a large number of liquid fractions of various sizes some of which differed only slightly in refractive index. In the second method, each "freeze" was separated into only two or three fractions, the cuts being made when the refractive index showed the most rapid change with the volume of liquid drawn off. The latter method was found to be the most rapid in practice, and a typical example of the course of this procedure is shown in Figure 6.

4. METHOD OF INTERLOCKING CRYSTALLIZATION WITH DISTILLATION

The fractional crystallization divided the material into a series of fractions ranging in refractive index from that of n-octane up to values considerably higher than that of the material as obtained from the distillation. The material with high index and low freezing point was redistilled while the fractions with low index, which were too small for further crystallization were added to the appropriate crystallization fractions from the next lot of new material.

The chart shown in Figure 7 outlines the actual course of the work. It is to be read from the top down. Thus, the first row of circles represents the cuts from the third distillation in glass stills. Only a part of the 124° to 125° fraction was crystallized and the crystalline portion was saved until more material was obtained from the fourth distillation before further fractionation. This is indicated by the broken line leading to the right from the small square under the 124° to 125° fraction.

The second row of large circles represents the fractions of the fourth distillation. Four fractions of this disillation were crystallized, and the crystalline fractions united for the systematic fractional crystallization represented by the large square, A, at the right. Figure 6 is typical of the process which this square represents. This crystallization produced 4 liters of product represented by the square, B_1, (fig. 7), and a series of residual fractions as explained before which are represented by the square, C_1.

Of the fifth distillation six cuts were fractionated. The residual fractions, C_1, were worked into this fractionation for further treat-

[11] This apparatus is quite similar to that used by Kanolt in the determination of the viscosity of liquids. See B. S. Sci. Paper No. 520, p. 628; 1926.

ment. Two liters of product was obtained; C_2 represents the residual fractions too small for further work; and the circle, D_2, represents material of such low octane content that fractionation was impractical. The broken line leading back from D_2 toward the distillation indicates that the material was redistilled, and added to the corresponding fractions of the sixth distillation. The remainder of the chart is to be interpreted in the same way.

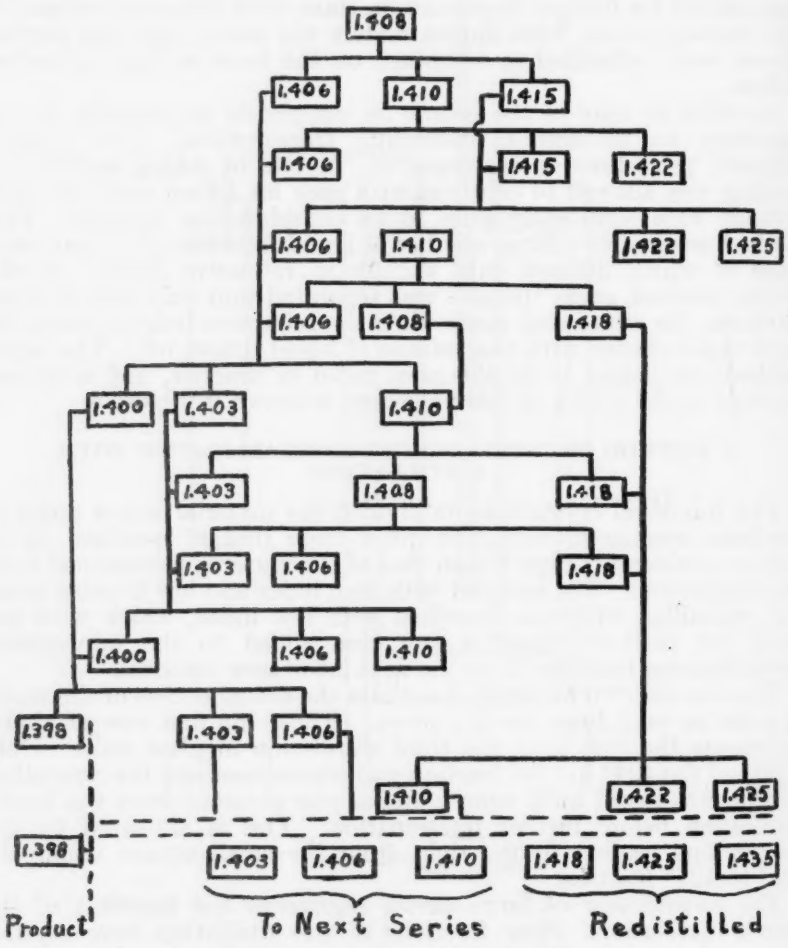
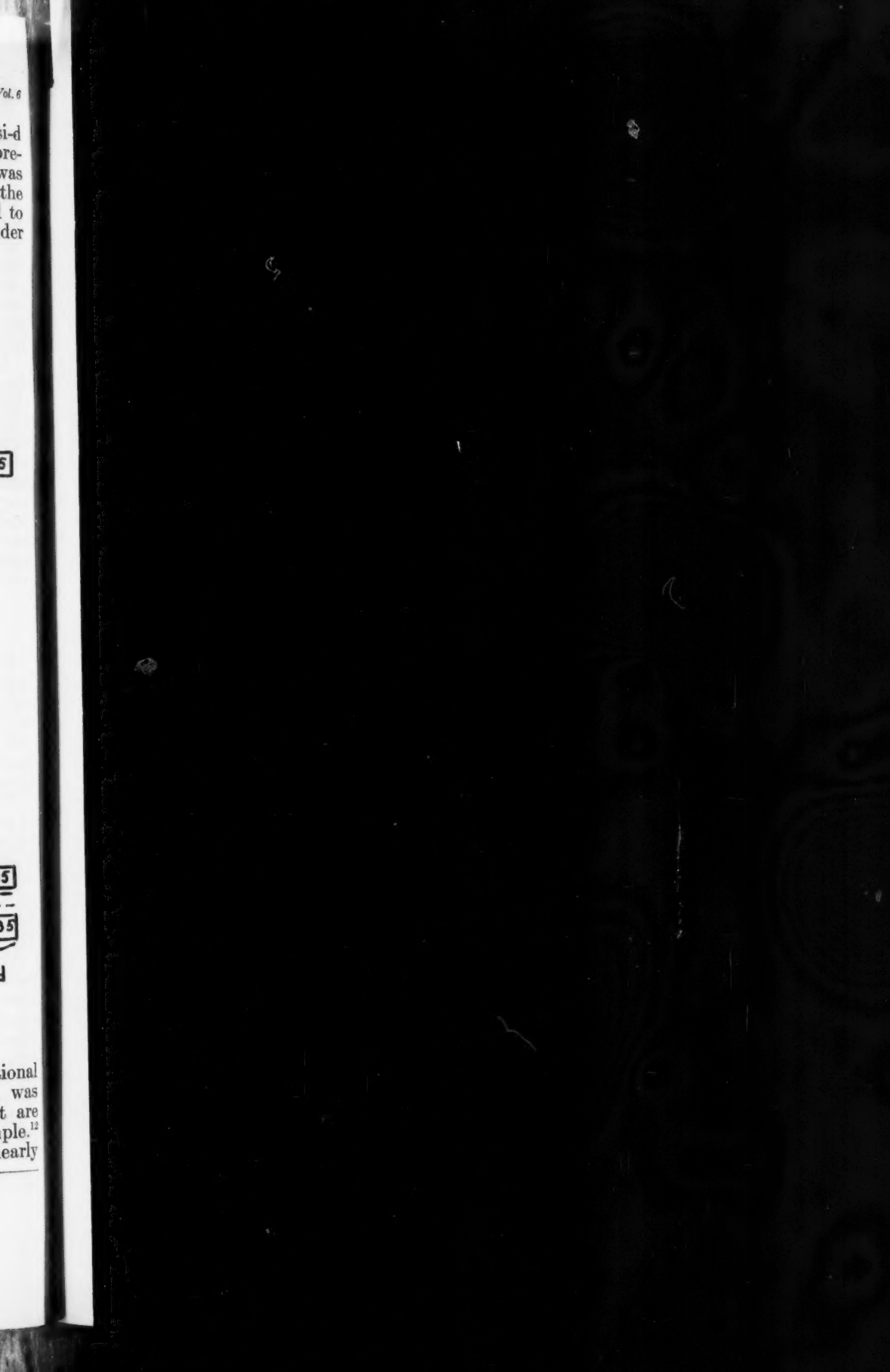


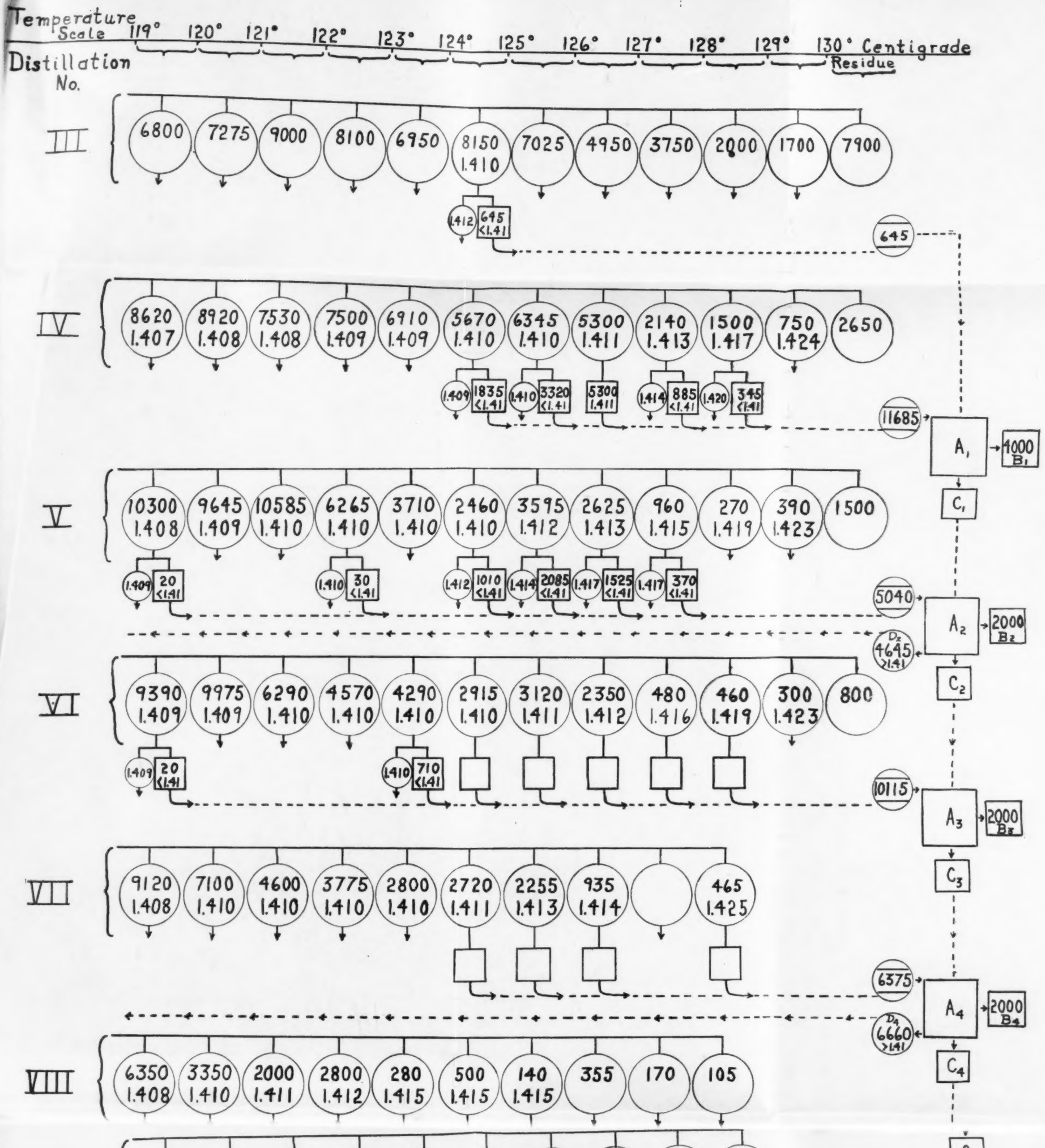
FIGURE 6.—*A typical fractional crystallization*

III. PROPERTIES OF THE PRODUCT

After 11 distillations in glass stills interspersed with five fractional crystallizations, 12.75 liters of approximately pure *n*-octane was collected. In Table 1 the physical properties of the product are compared with those of an especially purified synthetic sample.[12] The properties were measured with the same apparatus and as nearly

[12] Prepared by B. J. Mair, research associate, National Bureau of Standards.




Temperature Scale
119° 120° 121° 122° 123° 124° 125° 126° 127° 128° 129° 130° Centigrade
Residue
Distillation No.
III
6800 7275 9000 8100 6950 8150 1.410 7025 4950 3750 2000 1700 7900
1.412 645 <1.41
645
IV
8620 1.407 8920 1.408 7530 1.408 7500 1.409 6910 1.409 5670 1.410 6345 1.410 5300 1.411 2140 1.413 1500 1.417 750 1.424 2650
1.409 1835 <1.41
1.410 3320 <1.41
5300 1.411
1.414 885 <1.41
1.420 345 <1.41
11685
A1
4000 B1
C1
V
10300 1.408 9645 1.409 10585 1.410 6265 1.410 3710 1.410 2460 1.410 3595 1.412 2625 1.413 960 1.415 270 1.419 390 1.423 1500
1.409 20 <1.41
1.410 30 <1.41
1.412 1010 <1.41
1.414 2085 <1.41
1.417 1525 <1.41
1.417 370 <1.41
5040
A2
2000 B2
D2 4645 >1.41
C2
VI
9390 1.409 9975 1.409 6290 1.410 4570 1.410 4290 1.410 2915 1.410 3120 1.411 2350 1.412 480 1.416 460 1.419 300 1.423 800
1.409 20 <1.41
1.410 710 <1.41
10115
A3
2000 B3
C3
VII
9120 1.408 7100 1.410 4600 1.410 3775 1.410 2800 1.410 2720 1.411 2255 1.413 935 1.414 465 1.425
6375
A4
2000 B4
D4 6660 >1.41
C4
VIII
6350 1.408 3350 1.410 2000 1.411 2800 1.412 280 1.415 500 1.415 140 1.415 355 170 105
C5

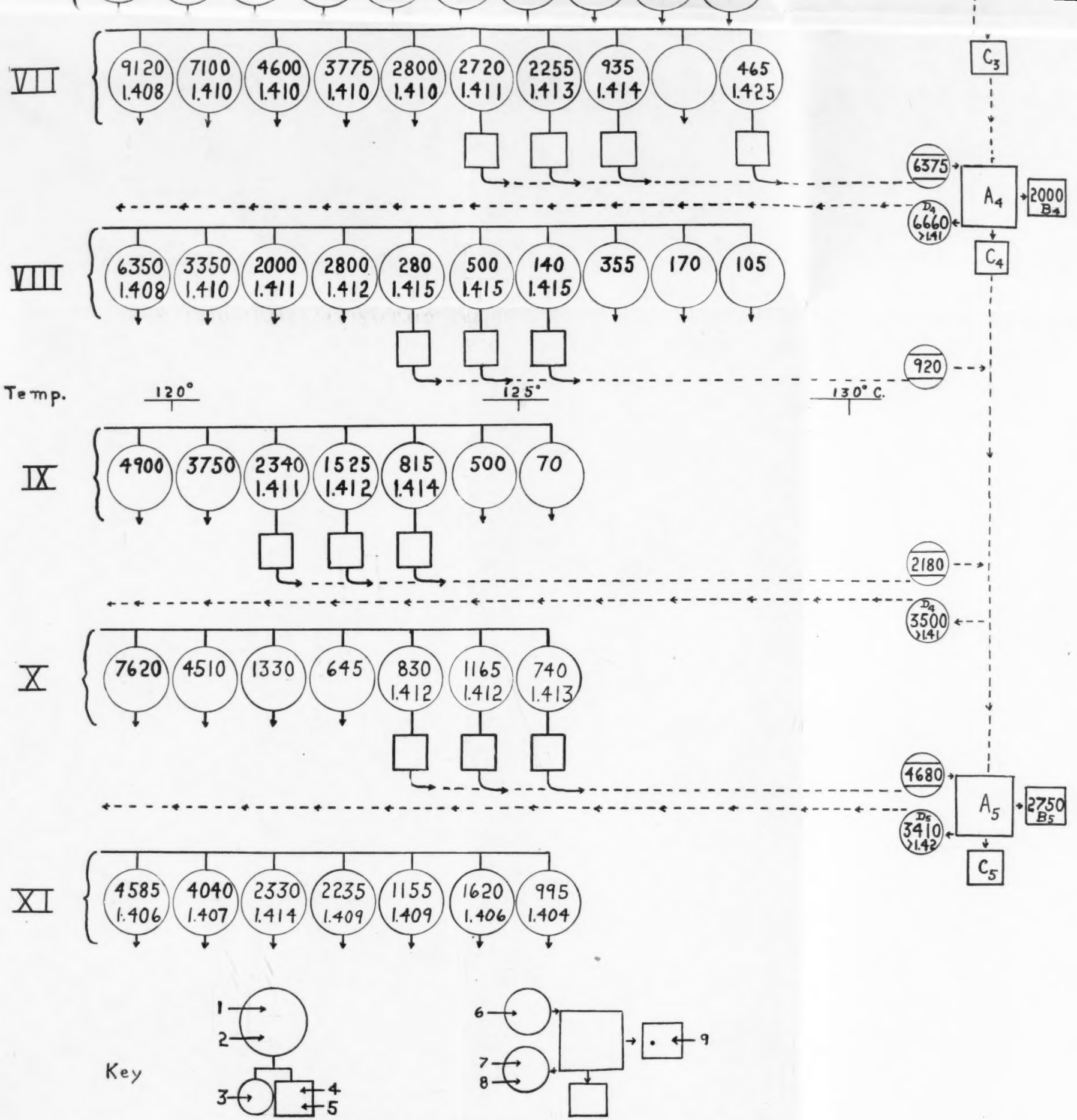


FIGURE 7.—*Method of interlocking crystallization with distillation*

1, volume of distillate; 2, refractive index of distillate; 3, refractive index of mother liquid; 4, volume of crystalline fraction; 5, refractive index of crystalline fraction; 6, total volume of crystalline fraction taken from distillation; 7, volume of material returned to distillation; 8, refractive index of material returned to distillation; 9, volume of product

36798°—31. (Face p. 384.)

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as possible in the same way in each case, and for purposes of comparison should be reliable to the number of significant figures given. No attempt was made to reach the ultimate purity obtainable on all the material, but rather to obtain the maximum quantity of material of approximate purity. As a result, the various lots differ somewhat in purity. In two instances, however, samples of much higher purity were produced, one by physical separation and the other by chemical destruction of the impurities. The first of these, Lot VII, was collected in the process of one of the regular fractionations by allowing the equilibrium melting to continue longer than usual. The second one, Lot VIII, was obtained by treating 200 ml of Lot II with 300 ml of chlorosulphonic acid and stirring continuously for seven days. This treatment has been shown to destroy normal paraffin hydrocarbons more slowly than the other classes so that almost pure normal paraffins can be obtained from mixtures in which the other classes are present as minor constituents.[13]

TABLE 1.—*Comparison of properties of n-octane obtained from petroleum with the properties of synthetic n-octane*

Material	Volume	n_D^{20}	Comparative boiling point 760 mm Hg	Initial freezing point	Mole percentage *n*-octane	Molecular weight [1]
			°C.	°C.		
Synthetic *n*-octane		1.3970	125.7	−56.9	100	(114.1).
Lot I	2,000	1.3985	125.4	−58.0	94.6	
Lot II	2,000	1.3990	125.3	−58.0	94.6	113.2±0.3.
Lot III	2,750	1.3980	125.4	−58.2	93.7	
Lot IV	2,000	1.3985	125.4	−57.7	96.0	
Lot V	2,000	1.3975	125.5	−57.6	96.5	
Lot VI	2,000	1.3975	125.5	−57.7	96.0	113.9±0.3.
Lot VII	100	1.3970	125.5	−57.2	98.5	
Lot VIII	77	1.3970	125.4	−57.1	99.1	

[1] Molecular weight determinations made by M. M. Hicks-Bruun, National Bureau of Standards.

The mole percentage of *n*-octane in each sample was calculated from the difference in the initial freezing point of the sample and that of the synthetic material. The heat of fusion was taken to be 40.3 cal./g.[14]

From the maximum and minimum values of the molecular weight of Lot II and the mole percentage of *n*-octane calculated from the freezing point, the average molecular weight of the contaminating material is shown to lie between 90 and 103.

The cooling curves from which the freezing points were determined are reproduced in Figure 8 because they offer considerable evidence regarding the purity of the samples. Figure 9 is a photograph of the long, prismatic crystals obtained by slow cooling.

After completing the above tests Lots I to VI, inclusive, were distilled through a 30-foot column packed with jack chain. Of the material, 93.3 per cent distilled between 125° and 126° C.; 4.2 per cent distilled below 125° C.; and 2.5 per cent distilled above 126° C.

[13] Shepard and Henne, Ind. Eng. Chem., **22**, p. 356; 1930.
[14] Parks and Todd, Ind. Eng. Chem., **21**, p. 1235; 1929.

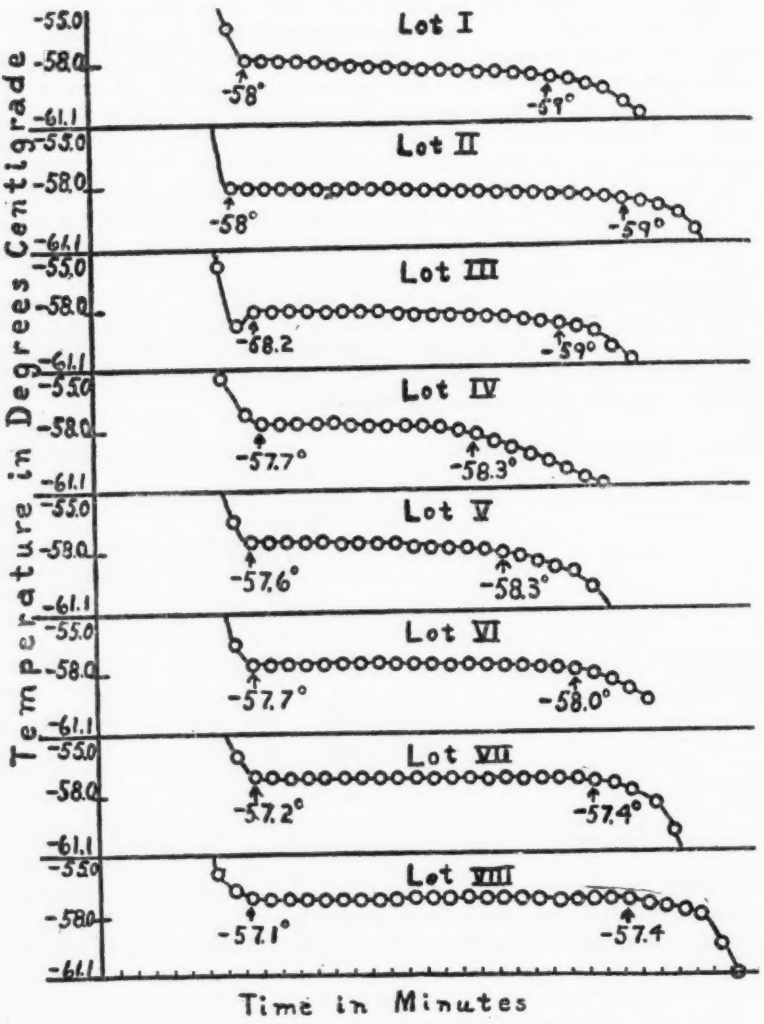

FIGURE 8.—*Freezing curves of n-octane*

IV. OCTANE CONTENT OF THE CRUDE OIL

After making reasonable allowance for losses incurred in the various operations it is safe to conclude that the *n*-octane content of the crude oil was not less than 1.0 per cent.

WASHINGTON, December 26, 1930.

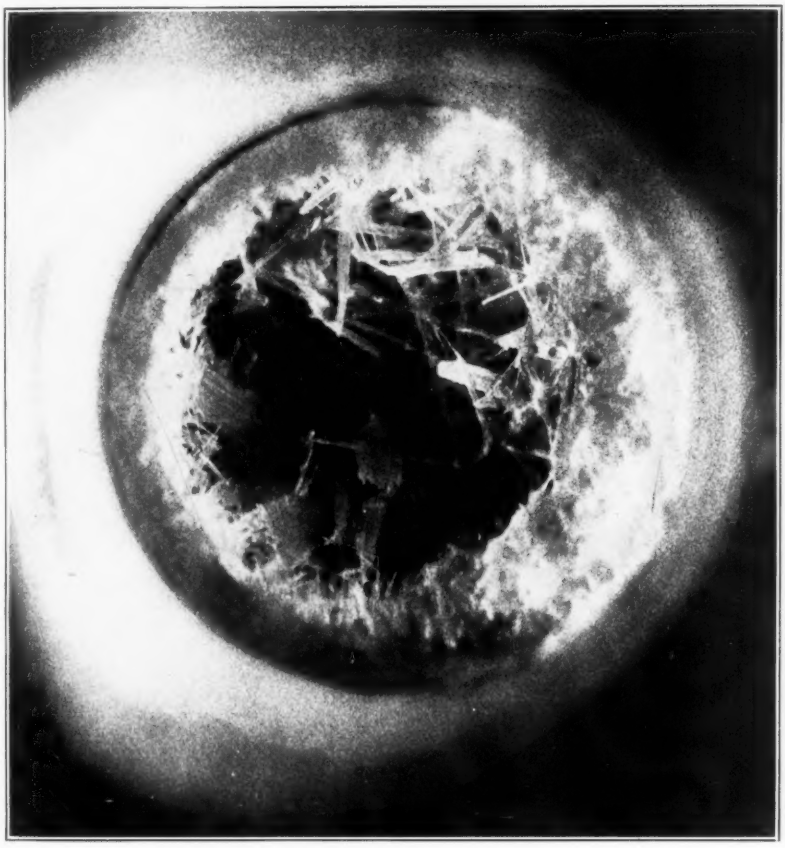

FIGURE 9.—*Photograph of n-octane crystals.* × 4

FURTHER MEASUREMENTS OF PROPELLER FAN CHARACTERISTICS

By P. S. Ballif and H. L. Dryden

ABSTRACT

The characteristics of a 4-blade propeller fan 8 feet in diameter operating under conditions approximating those encountered in cooling towers have been determined for comparison with the performance of 2-blade propeller fans, thus establishing experimentally the effect of increasing the number of blades. In addition, the characteristics of a 2-blade fan 9 feet 11 inches in diameter operating in a duct 10 feet in diameter have been measured for determining the effect of modifying the conditions of installation. Each fan was tested for two conditions of operation—when the fan was operated as a blower, and when the fan was exhausting air from the duct.

The results have been compared with the performance of an 8-foot, 2-blade propeller fan of approximately the same pitch/diameter ratio. The chief effect of increasing the number of blades is to reduce the speed of rotation required to meet given conditions. A faired entrance for the blower arrangement improves the performance of the fan.

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I. INTRODUCTION

In an earlier paper [1] an account has been given of some measurements of the characteristics of seven 2-blade propeller fans as applied to cooling tower installations. It was found that 2-blade propeller fans are suitable for moving large volumes of air against pressures that are not greatly in excess of 1 inch of water, but for greater pressures the required speed of rotation becomes inconveniently large. It was pointed out that one method of overcoming this difficulty is to increase the number of blades.

This report presents the results of an extension of the investigation to the measurement of the characteristics of one 4-blade propeller fan 8 feet in diameter operating under the same conditions as in the previous tests (approximately those encountered in cooling tower installations). The purpose of these measurements was to obtain data for comparison with the 2-blade fan characteristics as presented in Research Paper No. 193. In addition, the results of some measurements of the characteristics of a 2-blade propeller fan 9 feet 11 inches in diameter operating in a duct 10 feet in diameter are given to illustrate the effect of modifying the conditions of installation.

[1] B. S. Jour. Research, 5 (RP193); 1930.

II. APPARATUS

The equipment and methods of experiment are the same as those described in the preceding paper, except that in the case of the larger fan the inlet ring was removed (fig. 1) and an additional set of measurements was made in which the fan was used as a blower and a faired section was added to the entrance. (Fig. 2.) In the blowing experiments, except for this one series of observations, the entrance was never faired; for the exhaust experiments the entrance was always faired.

The 4-blade fan is 8 feet in diameter and the nominal pitch is 4 feet. The measured geometric pitch is given in Table 1 and the approximate shape and dimensions are shown in Figure 3.

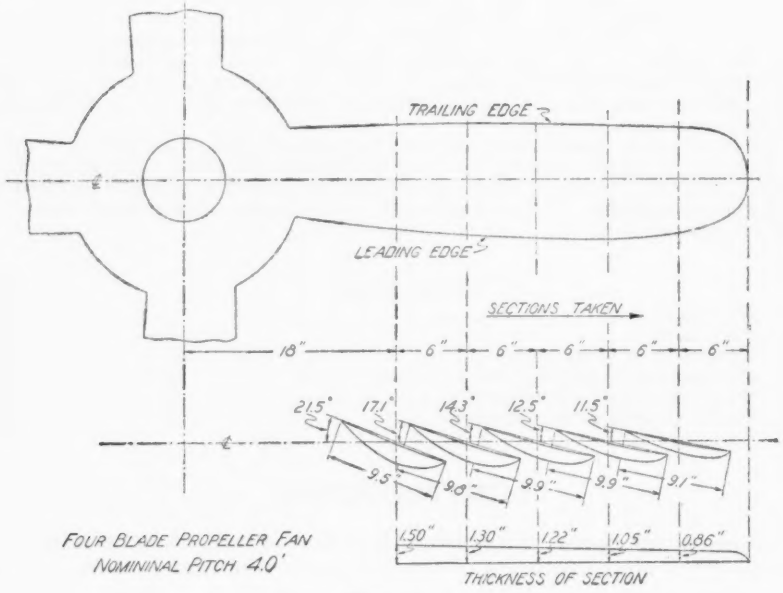

FIGURE 3

TABLE 1.—*Measured pitch of 4-blade fan*

Nominal Pitch 4 feet: Radius=distance from axis to point at which pitch is measured

	Radius (in feet)				
	1.5	2.0	2.5	3.0	3.5
Pitch (in feet)	3.72	3.86	4.00	4.19	4.45
Pitch/diameter ratio	.465	.483	.500	.524	.556

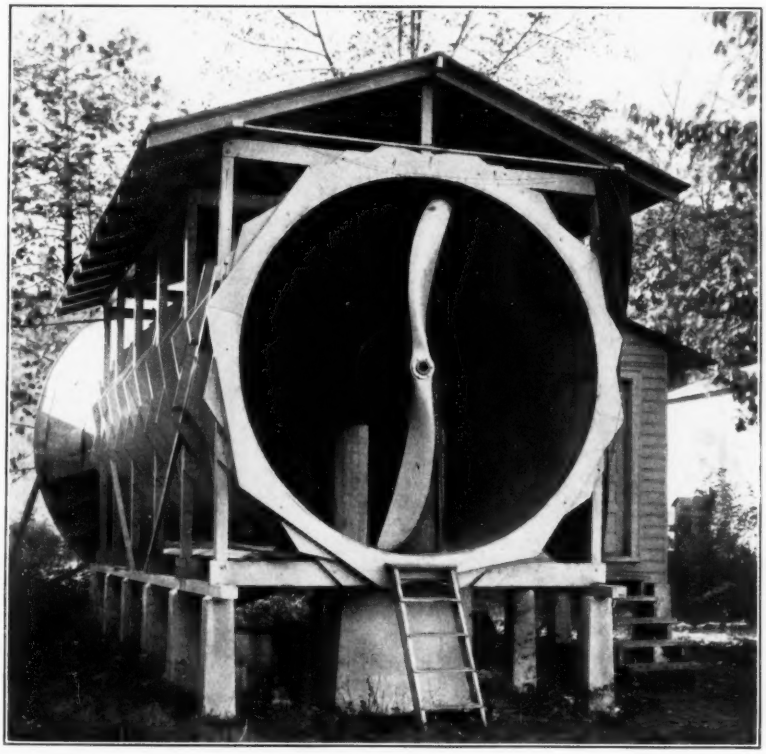

FIGURE 1.—*Test duct with inlet ring removed and 9-foot 11-inch fan in place*

FIGURE 2.—*Test duct with faired entrance section for blower condition*

TABLE 2.—*Measured pitch of 2-blade fans*

Radius=distance from axis to point at which pitch is measured

	Radius (in feet)											
	1.5		2.0		2.5		3.0		3.5		4.0	4.5
	Fan											
	9 ft. 11 in.	8 ft.	9 ft. 11 in.	8 ft.	9 ft. 11 in.	8ft.	9 ft. 11 in.	8 ft.	9 ft. 11 in.	8 ft.	9 ft. 11 in.	9 ft. 11 in.
Pitch (in feet)	5.00	3.94	5.01	4.03	5.02	4.12	4.98	4.32	5.00	4.40	4.98	4.99
Pitch/diameter ratio	.504	.493	.505	.504	.506	.515	.502	.540	.504	.550	.502	.504

The 2-blade fan (fig. 4) is 9 feet 11 inches in diameter and the nominal pitch is 5 feet. The measured angles of the blade sections agreed with the nominal values within 0.1°. The measured geometric pitch is given in Table 2, which includes also, for comparison, data for the previously used 8-foot 2-blade fan of approximately the same pitch/diameter ratio. Figure 5 shows the approximate shape and dimensions of the 8-foot fan. All of the fans are constructed of laminated wood.

III. REDUCTION OF OBSERVATIONS

To facilitate the estimation of the performance of similar fans when operating under similar conditions, the results are expressed in the form of coefficients defined as follows:

$$K_H = 10^8 \frac{H}{N^2 D^2}$$

$$K_Q = \frac{Q}{N D^3} \qquad (1)$$

$$K_P = 10^{12} \frac{P}{N^3 D^5}$$

$$\text{Efficiency} = \frac{5.2\ QH}{33{,}000\ P} = \frac{10^4 \times 5.2\ K_H K_Q}{33{,}000\ K_P}$$

where K_H is called the total pressure coefficient, K_Q the volume coefficient, K_P the power coefficient, and N = rotational speed (r. p. m.), D = diameter of fan (feet), Q = volume of air (cu. ft./min.), P = horsepower absorbed by fan, and H = change in total pressure produced by fan (inches of water); that is, the change in static pressure plus the increase (or minus the decrease) in the velocity pressure.

As explained in Research Paper No. 193 the pressure coefficient for the 8-foot fan operating as a blower is

$$K_H = 10^8 \frac{H_S}{N^2 D^2} + 4.13 K_Q^2$$

and for the exhaust condition

$$K_H = 10^8 \frac{H_S}{N^2 D^2} + 5.55 K_Q^2$$

where H_S is the departure of the static pressure in the duct from atmospheric pressure (in inches of water).

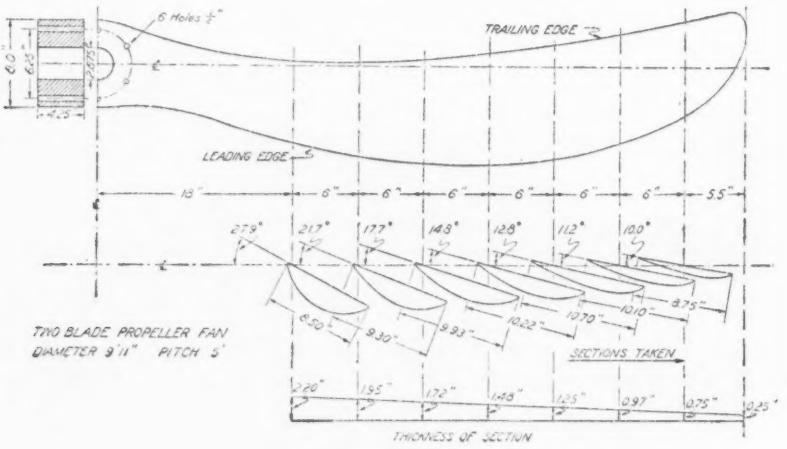

FIGURE 4

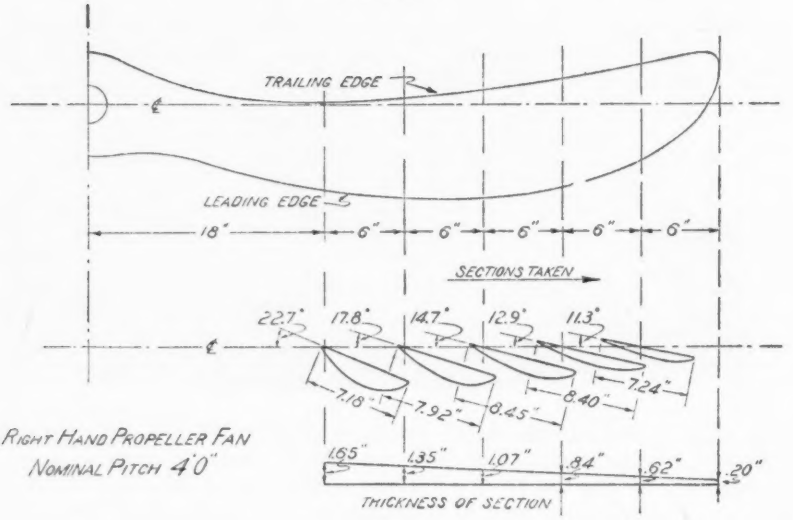

FIGURE 5

In the case of the 9-foot 11-inch fan for the blower condition, the air starts from rest at atmospheric pressure, and H is the excess of the total pressure in the 10-foot duct above that pressure. As D is 9 feet 11 inches, the increase in velocity pressure is

$$\frac{N^2 D^2}{10^8} (9.98 K_Q^2)$$

and

$$H = H_S + \frac{N^2D^2}{10^8}(9.98K_Q^2)$$

Hence,

$$K_H = 10^8 \frac{H_S}{N^2D^2} + 9.98K_Q^2$$

For the exhaust condition, the discharge velocity is the same as the velocity in the 10-foot duct, there is no change in the velocity pressure, hence

$$K_H = 10^8 \frac{H_S}{N^2D^2}$$

IV. COMPARISON OF THE PERFORMANCE OF 4-BLADE FAN AND 2-BLADE FAN

The results obtained for the 4-blade fan are summarized in Tables 3 and 4 and in Figures 6 and 7. For comparison we have included

TABLE 3.—*4-blade blower fan*

Pitch=4 feet; pitch/diameter ratio=0.50

585 r. p. m.				700 r. p. m.			
K_H	K_Q	K_P	Efficiency [1]	K_H	K_Q	K_P	Efficiency [1]
			Per cent				*Per cent*
0.997	0.3720	2.065	27.0	0.980	0.3705	2.122	27.2
2.371	.2840	2.240	46.5	2.357	.2890	2.330	46.0
2.787	.2405	2.185	47.1	2.805	.2385	2.274	47.1
3.606	.1524	2.057	42.0	3.786	.1445	2.086	41.5
4.155	.1048	1.885	35.7	4.162	.1063	1.973	36.3
5.640	0	1.728	0	5.610	0	1.810	0

[1] These values of efficiency were taken from smoothed curve.

Figures 8 and 9 (taken from Research Paper No. 193) which are the plotted results of the tests on the 2-blade fan of approximately the same pitch/diameter ratio. Table 5 gives the ratio of the characteristics of the two fans at several points. All of the ratios given apply to the particular fans compared. It should especially be noted that these fans differ both in blade outline and in blade area (see figs. 3 and 5), as well as in number of blades.

TABLE 4.—*4-blade exhaust fan*

Pitch=4 feet; pitch/diameter ratio=0.50

585 r. p. m.				700 r. p. m.			
K_H	K_Q	K_P	Efficiency [1]	K_H	K_Q	K_P	Efficiency [1]
			Per cent				*Per cent*
1.233	0.3005	2.115	27.9	1.257	0.3130	2.257	26.3
2.043	.2478	2.238	34.4	2.017	.2488	2.390	34.1
2.489	.2168	2.172	37.6	2.521	.2125	2.310	37.7
3.308	.1545	2.008	39.3	3.314	.1550	2.094	39.5
3.614	.1152	1.917	33.8	3.626	.1186	1.962	34.5
4.910	0	1.554	0	4.830	0	1.681	0

[1] These values of efficiency were taken from smoothed curve.

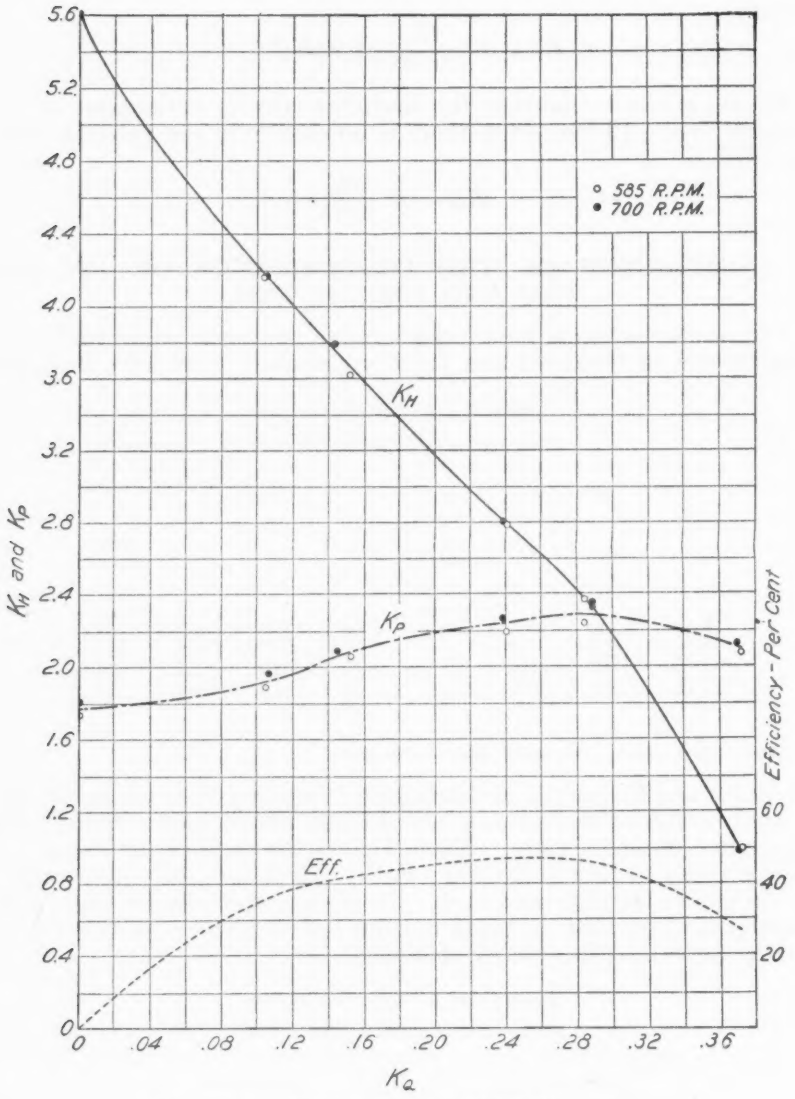

FIGURE 6.—*Characteristics of 4-blade blower fan*

Diameter, 8 feet; pitch, 4 feet; pitch/diameter ratio, 0.50

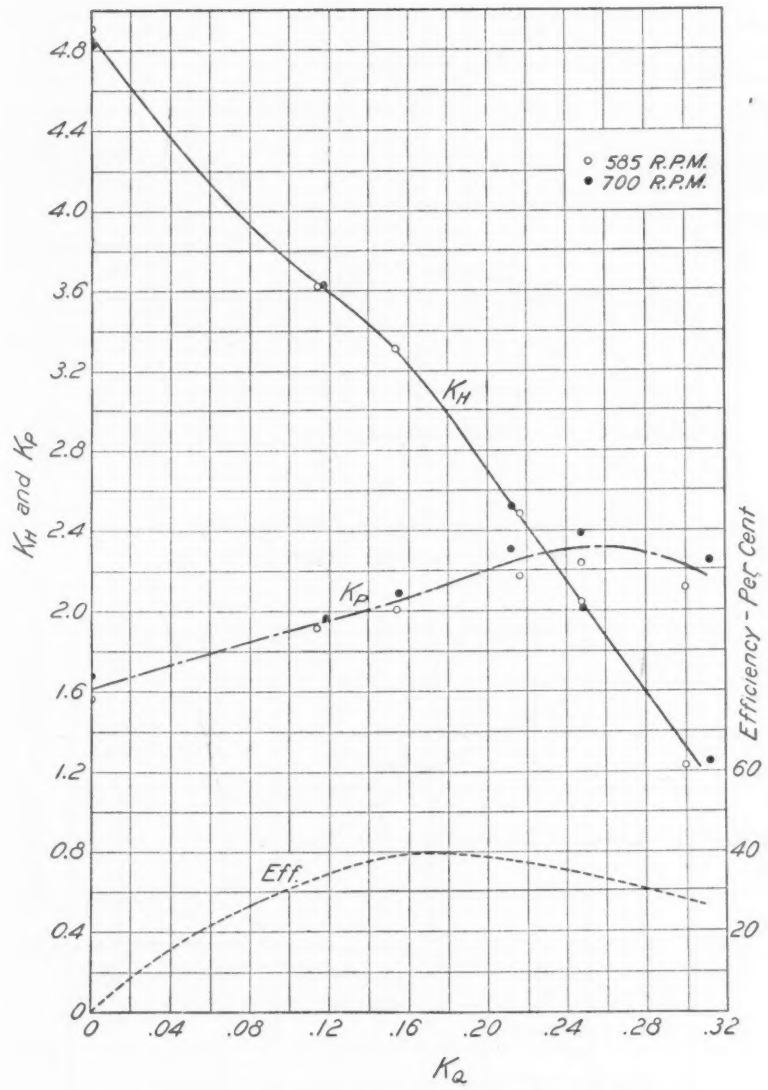

FIGURE 7.—*Characteristics of 4-blade exhaust fan*

Diameter, 8 feet; pitch, 4 feet; pitch/diameter ratio, 0.50

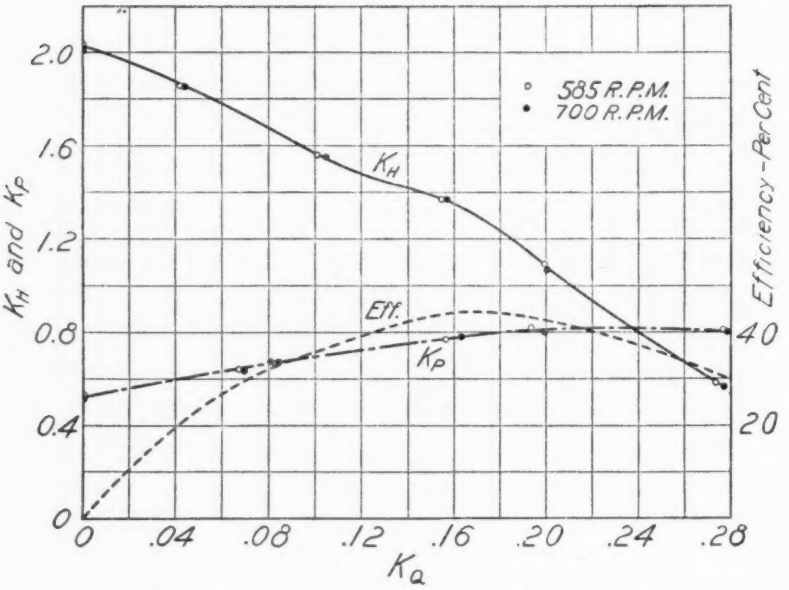

FIGURE 8.—*Characteristics of 2-blade blower fan*

Diameter, 8 feet; pitch, 4 feet; pitch/diameter ratio, 0.50

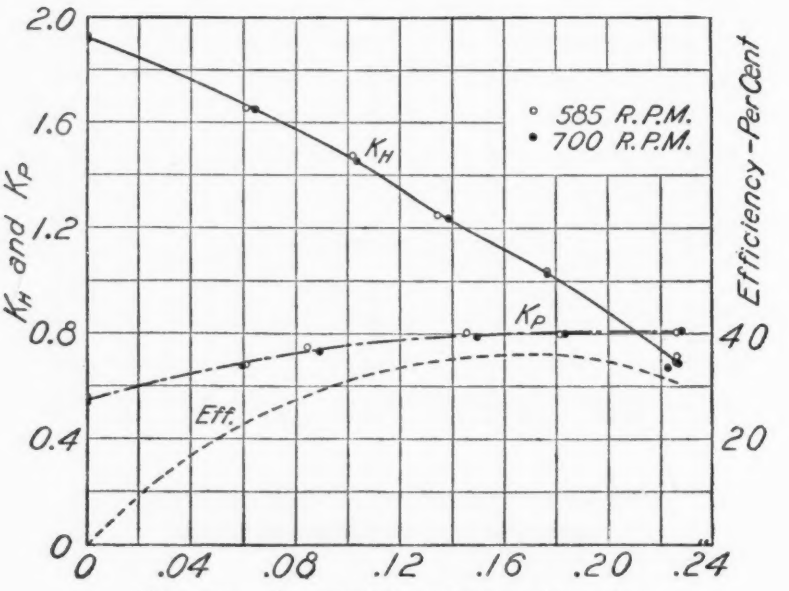

FIGURE 9.—*Characteristics of 2-blade exhaust fan*

Diameter, 8 feet; pitch, 4 feet; pitch/diameter ratio, 0.50

TABLE 5.—*Ratio of the characteristics of the 4-blade fan to those of the 2-blade fan*

Each fan was 8 feet in diameter and had the same pitch/diameter ratio (0.5)

	Condition	
	Blower	Exhaust
	4-blade÷2-blade	
Maximum volume [1]	1.34	1.35
Maximum pressure	2.78	2.53
Power at maximum volume	2.59	2.70
Power at maximum pressure	3.40	2.94
Volume at maximum efficiency	1.53	1.00
Pressure at maximum efficiency	2.02	2.93
Power at maximum efficiency	2.92	2.60
Maximum efficiency	1.07	1.08

[1] The value given for the maximum volume is that obtained with resistance in the duct, that caused by the honeycomb-partition and the motor; hence the values given may be slightly increased by reducing the duct resistance. It should be noted, however, that the curves can not be extrapolated to zero pressure, since H includes the pressure due to velocity.

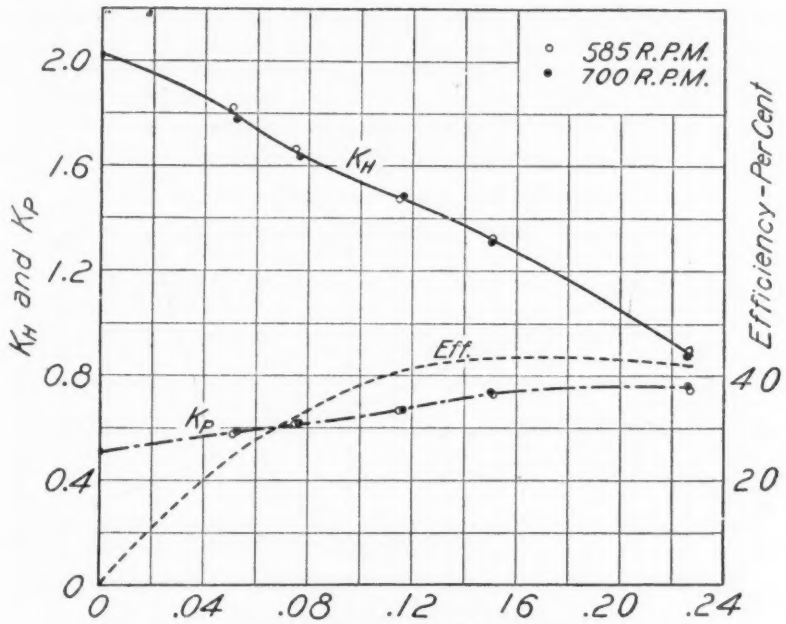

FIGURE 10.—*Characteristics of 2-blade blower fan*

Diameter, 9 feet 11 inches; pitch, 5 feet; pitch/diameter ratio, 0.50

V. EFFECT OF ENTRANCE CONDITION

The results for the 9-foot 11-inch 2-blade fan are summarized in Tables 6, 7, and 8 and in Figures 10, 11, and 12. On comparing Figure 10 with Figure 8, the two sets of curves are seen to be in fairly good agreement, the pressure and the power for the 8-foot fan being 2 or 3 per cent higher throughout most of the range. On comparing

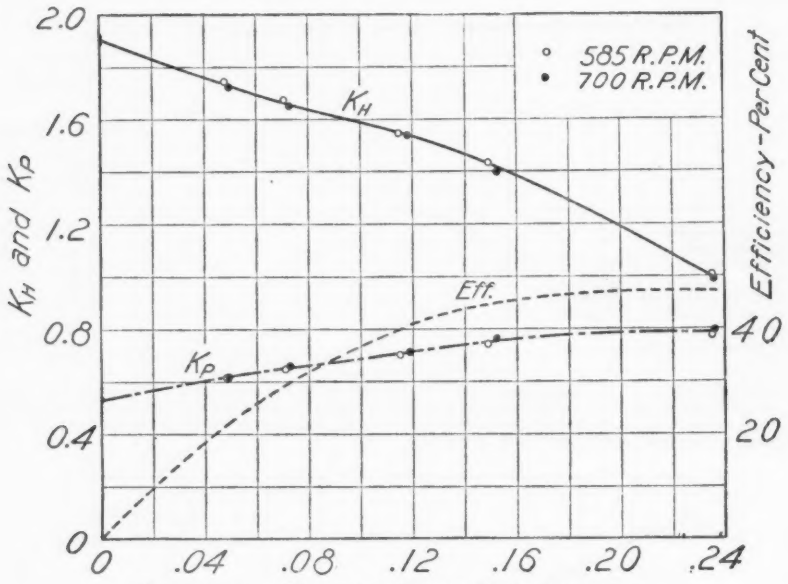

FIGURE 11.—*Characteristics of 2-blade exhaust fan*

Diameter, 9 feet 11 inches; pitch, 5 feet; pitch/diameter ratio, 0.50

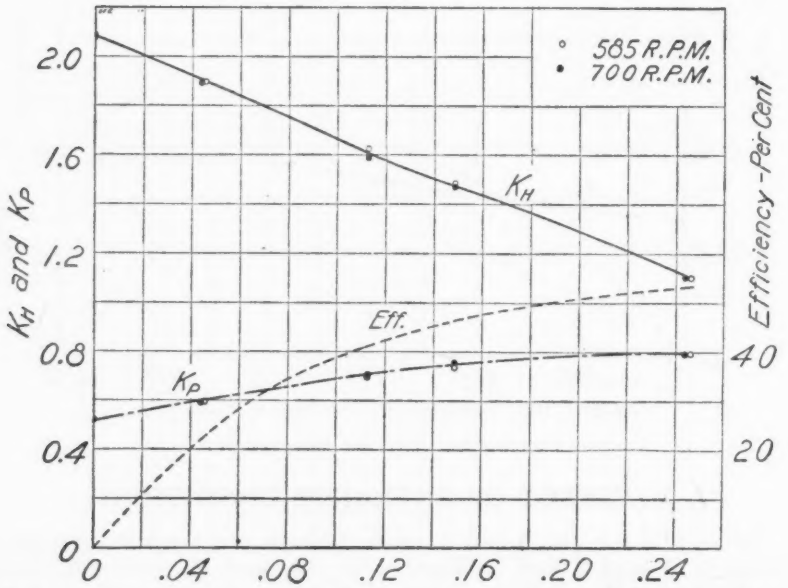

FIGURE 12.—*Characteristics of 2-blade blower fan with faired entrance section*

Diameter, 9 feet 11 inches; pitch, 5 feet; pitch/diameter ratio, 0.50

Figure 10 with Figure 12, we see that the chief effect of the faired entrance section is to increase the value of the pressure coefficient; at maximum volume the increase is about 25 per cent. It also increases the power coefficient by 1 or 2 per cent over most of the range, and the efficiency at maximum volume from 42 per cent to about 53 per cent.

On comparing Figure 11 with Figure 9, it is seen that, for the exhaust condition, the pressure produced at maximum volume by the 9-foot 11-inch fan is about 50 per cent greater than that for the 8-foot fan of approximately the same pitch/diameter ratio; the power for the 9-foot 11-inch fan is from 2 to 5 per cent less than for the 8-foot fan, and the maximum efficiency is increased from 36 per cent to 47 per cent. In the case of the 9-foot 11-inch fan there was no inlet ring, and it is our opinion that the increase in efficiency is due to the absence of the inlet ring rather than to the increase in the diameter of the fan.

From the above comparisons it is readily seen that the entrance and exit conditions have an appreciable effect on the performance of the fans. For a duct 10 feet in diameter, an 8-foot fan mounted in an inlet ring to simulate the wall condition in cooling tower applications is nearly as efficient as a fan 9 feet 11 inches in diameter for the blower condition, but is much less efficient for the exhaust condition. The faired entrance section improves the performance when the fan is operating as a blower. No data were obtained for the exhaust condition without the faired entrance section.

TABLE 6.—*2-blade blower fan (straight entrance)*

Pitch=5 feet; pitch/diameter ratio=0.50

585 r. p. m.				700 r. p. m.			
K_H	K_Q	K_P	Efficiency [1]	K_H	K_Q	K_P	Efficiency [1]
			Per cent				*Per cent*
0.806	0.2270	0.741	42.0	0.868	0.2260	0.762	42.0
1.325	.1510	.721	43.0	1.304	.1505	.734	43.0
1.474	.1150	.663	40.2	1.483	.1170	.667	40.5
1.661	.0752	.616	32.0	1.634	.0770	.618	32.2
1.821	.0512	.577	24.8	1.777	.0524	.581	25.2
2.020	0	.502	0	2.020	0	.507	0

[1] These values of efficiency were taken from smoothed curve.

TABLE 7.—*2-blade exhaust fan*

Pitch=5 feet; pitch/diameter ratio=0.50

585 r. p. m.				700 r. p. m.			
K_H	K_Q	K_P	Efficiency [1]	K_H	K_Q	K_P	Efficiency [1]
			Per cent				*Per cent*
1.008	0.2352	0.773	47.2	0.988	0.2359	0.790	47.2
1.430	.1493	.739	44.5	1.396	.1524	.761	44.8
1.548	.1156	.698	40.0	1.537	.1188	.712	40.5
1.672	.0712	.641	29.2	1.647	.0734	.654	29.8
1.746	.0489	.610	22.0	1.729	.0498	.610	22.2
1.920	0	.530	0	1.888	0	.529	0

[1] These values of efficiency were taken from smoothed curve.

TABLE 8.—*2-blade blower fan (faired entrance)*

Pitch=5 feet; pitch/diameter ratio=0.50

585 r. p. m.				700 r. p. m.			
K_H	K_Q	K_P	Efficiency [1]	K_H	K_Q	K_P	Efficiency [1]
			Per cent				*Per cent*
1.101	0.2468	0.794	53.2	1.102	0.2440	0.798	53.1
1.486	.1490	.732	46.2	1.471	.1487	.758	46.2
1.627	.1128	.691	41.1	1.588	.1127	.707	41.1
1.899	.0463	.591	22.9	1.899	.0440	.595	22.0
2.073	0	.523	0	2.090	0	.521	0

[1] These values of efficiency were taken from smoothed curve.

VI. USE OF THE CHARACTERISTIC CURVES

The use of the characteristic curves can best be illustrated with an example: Suppose it is desired to have 34,200 cubic feet of air delivered against a total pressure of 0.5 inch of water using a 4-blade propeller fan of pitch/diameter ratio of 0.50 operating at maximum efficiency. What will be the speed of rotation, the diameter of the fan, and the power required?

From Figure 6 the values of the several coefficients at the point of maximum efficiency are found to be $K_H=2.71$, $K_Q=0.25$, and $K_P=2.26$.

Combining equations (1),

$$D^4=\frac{Q^2}{10^8}\frac{K_H}{H K_Q^2}$$

$$N=\frac{Q}{D^3 K_Q} \qquad (2)$$

Substituting the known values and solving, we get $D=5.64$ feet, and $N=762$ r. p. m.

The pitch is $5.64\times0.50=2.82$ feet.

From equations (1)

$$P=\frac{K_P N^3 D^5}{10^{12}}$$

which gives $P=5.72$ h.p.

In order to compare the above results with the performance of the 2-blade fan of approximately the same pitch/diameter ratio, the same problem may be solved. From Figure 8 the values of the coefficients at maximum efficiency are $K_Q=0.17$, $K_H=1.3$, and $K_P=0.78$. Substituting these values in equations (2) and solving gives D=5.7 feet, $N=1{,}087$ r. p. m., and $P=6.04$ h.p. The pitch is $5.7\times0.50=2.85$ feet. To get the same performance with the 2-blade fan it is necessary to increase the speed of rotation by about 33 per cent. The power absorbed is 5.6 per cent greater than for the 4-blade fan.

VII. SUMMARY

The operating characteristics of a 4-blade fan have been measured under conditions approximating those encountered in cooling towers. The characteristics of a 2-blade fan 9 feet 11 inches in diameter have been measured under more general conditions of operation, and the effect of fairing the entrance has been studied.

The results have been expressed in the form of pressure and power coefficients plotted against a volume coefficient in such a manner as to facilitate the estimation of the performance of similar fans of any diameter and speed of rotation when operating under similar conditions.

The 4-blade fan shows an increase in the range of pressure and volume coefficients as compared with the 2-blade fan of approximately the same pitch/diameter ratio. The effect of increasing the number of blades is to reduce the speed of rotation required to meet given conditions, and to increase the efficiency to a small extent.

For a duct 10 feet in diameter, an 8-foot fan mounted in an inlet ring to simulate the wall condition in cooling towers is nearly as efficient as a fan 9 feet 11 inches in diameter for the blower condition, but is much less efficient for the exhaust condition. The faired entrance section for the blower arrangement improves the performance of the fan.

WASHINGTON, January 7, 1931.

A PRECISION CRYOSTAT WITH AUTOMATIC TEMPERATURE REGULATION

By R. B. Scott and F. G. Brickwedde

ABSTRACT

A cryostat, which is an apparatus for maintaining constant low temperatures, has been designed and constructed for use in the temperature range from 0° to −170° C. In this range the temperature can be easily adjusted to any desired value and can be automatically maintained constant to within 0.001° C. It can also be used for maintaining temperatures at the boiling points of liquid oxygen, nitrogen, or air.

The cryostat bath is contained in a double walled cylindrical glass vessel surrounded by liquid air, the amount of refrigeration being controlled by varying the gas pressure between the walls. The cryostat liquid is circulated by a propeller in the bottom of a bakelite tube centrally located in the double walled vessel. The liquid is pumped up the inside of the bakelite tube, which is the constant temperature region of the cryostat, and down on the outside. By operating the propeller through a system of gears driven by a shaft on the outside of the bakelite tube, the whole space inside is available for experimental apparatus. Constant temperature is automatically maintained by a photo-electric cell thermo regulator which controls the current through a heating coil wound on the outside of the bakelite tube. Adequate circulation of the liquid, suitable heat insulation, and symmetrical distribution of the parts assure great uniformity of temperature. Nonflammable mixtures of liquids are used for the cryostat bath between 0° and −140° C. For lower temperatures liquid propane is used.

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I. INTRODUCTION

It frequently happens that the accuracy of the determination of a physical property is limited by the temperature variations of the supposedly constant temperature space in which the property is being measured. An apparatus has been developed which will automatically maintain any temperature, from 0° down to −170° C., constant and uniform to within 0.001° C. On account of limitations of temperature measurements and other factors this constancy and uniformity is as good as is required for practically all work in this range of temperatures.

Isolated temperatures can be maintained by substances undergoing a change of state at atmospheric pressure, and some limited ranges can be covered by controlling the pressure over boiling liquids.[1]

[1] K. Onnes, Leiden Communications Nos. 83, 94, and 123a.

It is, however, not only convenient, but for some work necessary that the temperature be adjustable to any desired point and be maintained constant automatically. For the interval near room temperatures this is relatively easy, but at higher and lower temperatures the problem becomes increasingly difficult.

Probably the most satisfactory and economical form of apparatus for use at low temperatures is a stirred liquid bath. Since liquids have rather high heat capacities, and, if well stirred will transfer heat quickly, they are well suited for maintaining constant and uniform temperatures. In providing refrigeration for the bath it is advantageous to have the heat leave the bath through a large surface, and to keep the refrigeration as constant as possible. Exposing a large cooling surface to the liquid reduces the temperature difference required to transfer a given amount of refrigeration, thereby making it possible to prevent the existence of cold spots in the bath which may occur if the refrigeration has to be transmitted through a small surface with a large temperature difference.

Since electric heating can be easily controlled through the action of a relay, the most convenient procedure for obtaining automatic temperature regulations is to provide a slight excess of refrigeration and to compensate for the excess with electric heating controlled by some thermosensitive device. The excess need be no greater than the combined maximum variations (1) of the refrigeration, (2) of the heat leakage into the bath from the warm exterior, and (3) of the energy dissipation in the bath. In order to obtain great constancy of temperature, these variations must be made small.

The constancy of temperature attainable also depends upon other factors which influence the response of the regulating device. These factors may be summarized briefly as follows: (1) Thermal lag in the thermosensitive element of the regulator, (2) time lags in the response of the regulator to changes in its thermosensitive element, (3) thermal lags in the heating and cooling elements, and (4) a time-lag effect which depends upon the velocity of circulation of the liquid and the relative positions of the heating and cooling surfaces with respect to the thermosensitive element. It is important that the temperature be constant with respect to time, but it is equally important that the temperature be uniform throughout the region of the bath in which the experimental apparatus is placed.

With these principles in mind a cryostat was designed and constructed for use with liquid air as the refrigerant. The refrigeration was applied and controlled by a method previously used by Rothe [2] and by Keyes, Taylor, and Smith,[3] namely, by surrounding the Dewar flask which holds the constant temperature bath with another Dewar filled with liquid air and controlling the refrigeration by varying the gas pressure between the two walls of the inner Dewar which is connected to a vacuum system. This method was selected in preference to other methods which might have been used because the refrigeration can be easily controlled, and by maintaining a constant liquid air level in the outer Dewar, which can be done automatically, the refrigeration remains very constant without further attention.

[2] Rothe, Zeitschrift für Instrumentendunde, **22**, pp. 14-21; 1902.
[3] Keyes, Taylor, and Smith, J. Math. & Phys. M. I. T., **1**, p. 211; 1922.

II. DESCRIPTION OF THE CRYOSTAT

A vertical section of the cryostat is shown to scale in Figure 1. It consists of an inner Dewar flask *D*, which contains the bath, surrounded by liquid air in the outer Dewar flask *C*. The inner flask is supported upon the metal ring *G*, which is connected by three copper-nickel alloy tubes *E* to the top plate *A*. The outer flask is supported from below on a pedestal which can be raised or lowered.

The refrigeration is controlled by varying the gas pressure between the walls of the inner Dewar *D*, which is connected by means of the side tube *M* to a vacuum system shown at *A* in Figure 2. In order to thermostat the cryostat at temperatures below $-160°$ C., hydrogen or helium is used between the walls. Very low pressures, or high vacua, requiring the use of a mercury diffusion pump are necessary for maintaining temperatures near 0° C. The pressure for maintaining any temperature is not critical. Excess refrigeration resulting from a higher pressure than is needed to maintain a temperature can be compensated for with a supply of heat generated by an electric current flowing through a heating coil immersed in the cryostat bath. The automatic thermoregulator compensates for small changes in the refrigeration, heating current supply, and the flow of heat into the cryostat from the outside. Because the stirring is vigorous, and the heating and cooling surfaces are near each other, compensating for excess refrigeration with electrical heating does not affect either the constancy or the uniformity of the temperature. A considerable change of temperature can be easily and quickly effected by varying the current through the heating coil in the liquid bath without the necessity of changing the pressure between the walls of the Dewar. Gas pressures between the walls of the inner Dewar are maintained by the use of a stopcock or mercury cut-off.

As far as possible, the nonflammable mixtures recommended by C. W. Kanolt [4] are used for the cryostat bath liquid. For temperatures down to $-75°$ C. the liquid used is the eutectic mixutre of carbon tetrachloride and chloroform (49.4 per cent, by weight, of CCl_4 and 50.6 per cent of $CHCl_3$), which has a freezing point of $-81.4°$ C. as determined by Kanolt. For temperatures between $-75°$ and $-140°$ C. a 5-component mixture containing 14.5 per cent of chloroform, 25.3 per cent of methylene chloride, 33.4 per cent of ethyl bromide, 10.4 per cent of transdichloroethylene, and 16.4 per cent of trichloroethylene was used. This mixture freezes at about $-150°$ C.

At temperatures below $-140°$ C. the nonflammable liquids become so viscous that they can not be readily stirred. For this lower range the liquid used is commercial propane, which is sold for domestic gas heating under various trade names. The propane, which is a gas at atmospheric pressure and room temperature, is compressed into steel cylinders and liquefied at a pressure of about 150 lbs./in.^{2} It can be liquefied at atmospheric pressure by running it through a copper coil immersed in liquid air. Its boiling point is about $-44°$ C., and it remains liquid down to liquid air temperatures. It is, however, highly flammable and its use is attended with some danger. It is recommended that pyrex glass or metal Dewars be used, and precautions be taken to prevent the mixing of the liquid air and

[4] C. W. Kanolt, B. S. Sci. Paper No. 520; March, 1926.

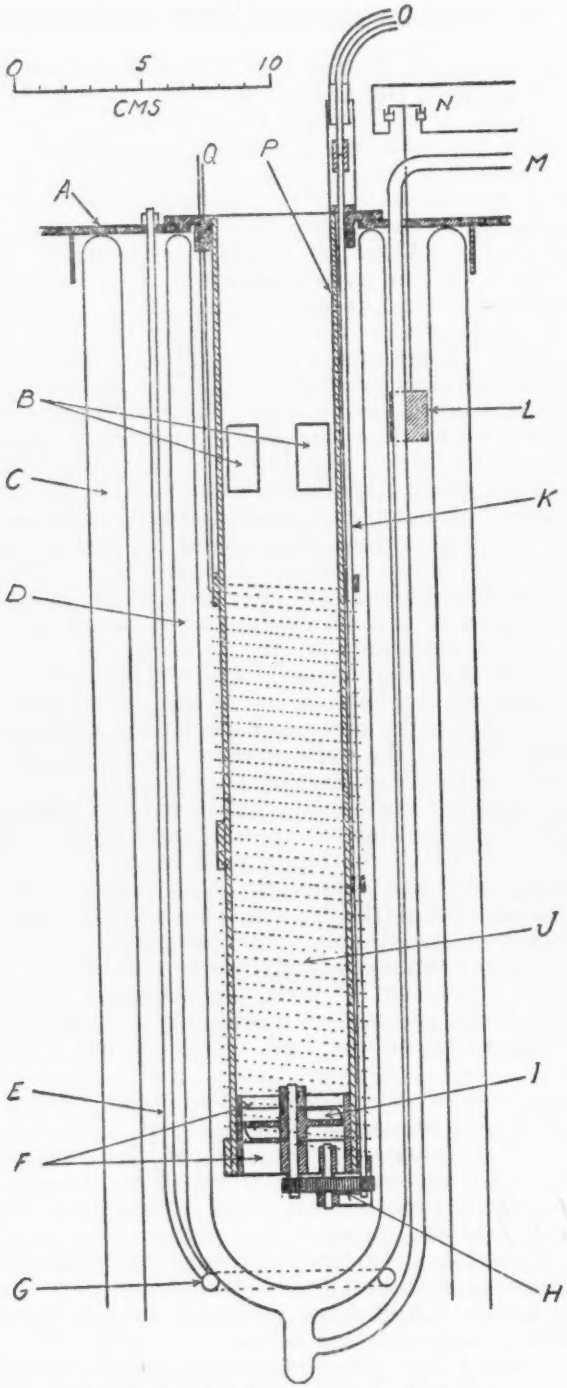

FIGURE 1.—*Vertical section of the cryostat*

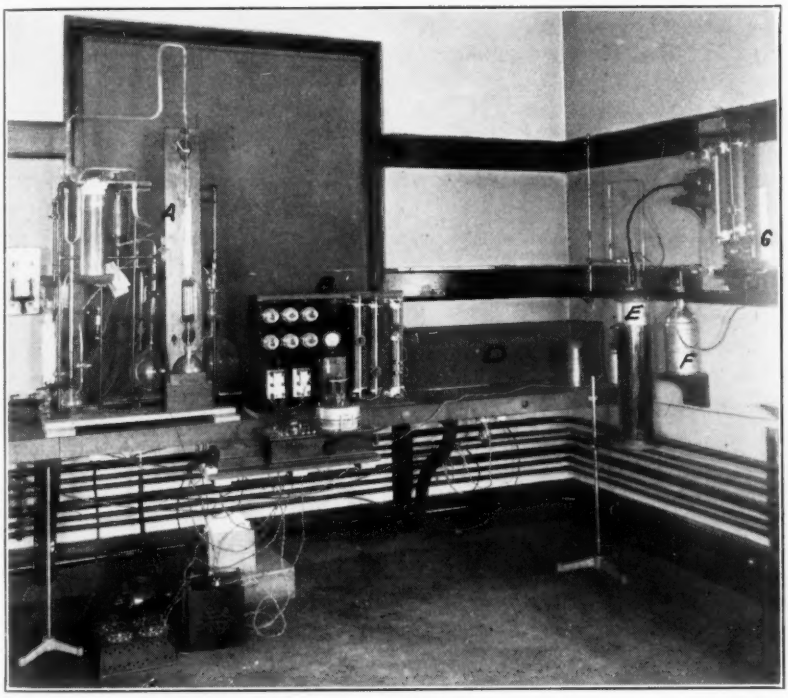

FIGURE 2.—*The cryostat and accessory apparatus*

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propane in case the Dewars break. If liquid nitrogen is available, it should be used instead of liquid air for the refrigerating liquid.

The cryostat bath liquid is circulated by a propeller *I* (see fig. 1) which revolves in the bottom of a bakelite tube *P* in such a direction that the liquid passes up through the inside of the bakelite tube and down on the outside. To permit this circulation, four windows *B*, 2.5 cm long, were cut in the bakelite tube. In order that the liquid at the surface of the bath shall be drawn away as its temperature is changed by the heat conducted in from the warm exterior, the liquid level is kept below the top of the windows. The propeller is driven at a speed of about 400 revolutions per minute by a system of three gears *H* driven by a shaft *K* connecting to a motor through a flexible shaft *O*. Three vertical vanes *F* support the bearings for the propeller and idler gear shafts and improve the circulation by preventing a whirling motion of the liquid above and below the propeller. Although gears made of brass running against stainless steel were found satisfactory, a combination of metal against bakelite was found to be quieter.

In the beginning trouble was experienced with a wearing away of the bearings and the shafts rotating in them, because the bearing surfaces were not lubricated, and the cryostat bath liquids attacked the bearing surfaces and formed substances on them that acted as abrasives. Several different combinations of metals were tried, and Monel metal shafts turning in a high lead (85 per cent) babbitt were used. New bearings are first "run in" with a good lubricating oil, cleaned with alcohol and rubbed with dry graphite before assembling for use.

The stirring mechanism can be quickly and easily taken apart and reassembled, which is desirable, as this must be done occasionally when ice collects in the gears.

The heating coil *J*, shown by dotted lines, is made of No. 22 B. & S. gage Nichrome wire and has a resistance of about 30 ohms. The bare wire is wound bifilarly on a form which fits on the stirrer tube *P*, its ends terminating at the top in the leads *Q* which connect to the thermoregulator. The form is made from a bakelite tube by cutting wide slots in its walls, leaving six strips about 1 cm. wide and supporting rings at the ends and center. Notches were cut in the strips to keep the wire from slipping. Lag in the heater is reduced by this support and manner of winding which separates the heater coil from the stirring tube and allows the bath liquid to circulate on all sides of the wire. By distributing the heater instead of concentrating it in a small part of the bath, the existence of hot spots in the cryostat is prevented. It is advantageous in compensating for a large excess of refrigeration, over that needed to maintain a desired temperature, to have the heating surface close to and distributed over the refrigerating surface. This, together with the vigorous stirring, makes it possible to operate under such conditions without affecting the constancy or uniformity of temperature in the constant temperature space.

The level of the liquid air in the outer Dewar is kept constant by means of an automatic constant level device.[5] The float *L* operates through the contacts *N* and relay *R*, a solenoid-operated valve *V*

[5] See Scott and Brickwedde, An Automatic Constant Level Device, Rev. Sci. Inst. (in press).

opening and closing a low-pressure air supply to the flask *F*, as shown diagrammatically in Figure 3. Due to the splashing and boiling of the liquid air, only a small amount is added each time the valve operates, and the level does not vary more than 1 or 2 millimeters.

The thermoregulator used is similar to a thermoregulator previously described by Southard and Andrews [6] and is diagrammatically represented in Figure 4. The thermosensitive sensitive element of the regulator is a 10-junction thermocouple which is represented by a

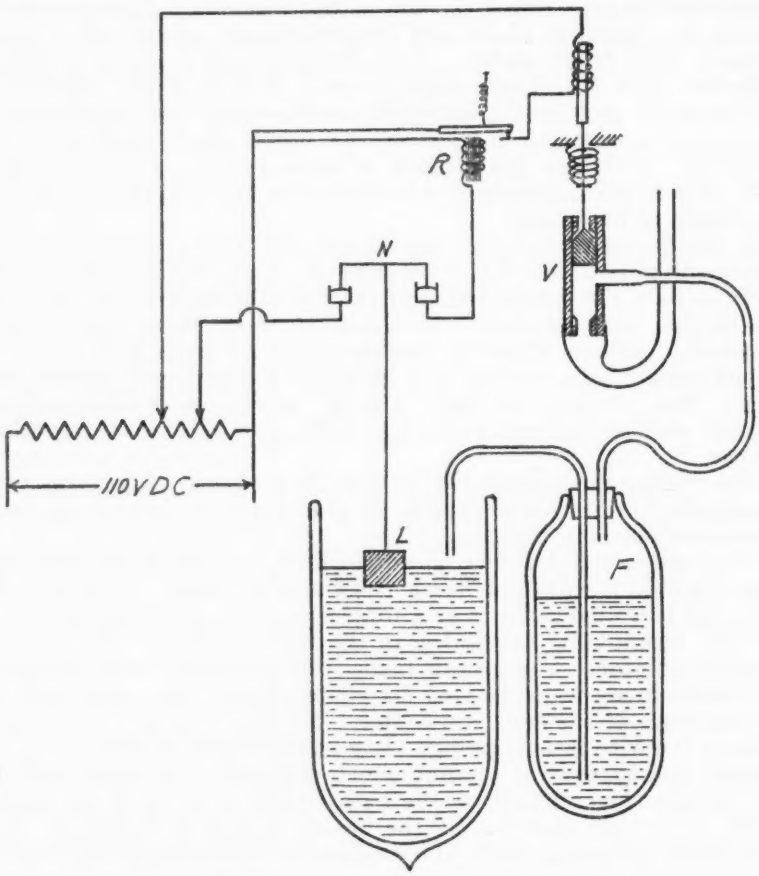

FIGURE 3.—*Diagram of the constant level device*

simple thermocouple *T*. One set of junctions spread out fanlike is placed just above the propeller, the external junctions being in an ice bath. The two leads of the multiple junction thermocouple are connected to a Leeds & Northrup, type K potentiometer *P* which may be set to the electromotive force of the thermocouple corresponding to the desired temperature. The potentiometer is balanced and used in much the same manner it would be used to measure the temperature of the cryostat with a thermocouple. Although a potentiometer is

[6] Southard and Andrews, J. Frank. Inst., **207**, pp. 323–339; 1929.

convenient, it can be replaced by an inexpensive circuit made up of adjustable resistances which will perform the same function as the potentiometer; that is, of balancing the electromotive force of the 10-junction thermocouple with a potential difference across a resistance through which a current flows. To the potentiometer is connected a Leeds & Northrup, type R galvanometer G having a resistance of about 40 ohms. An image of the straight filament of a lamp L is formed by the concave galvanometer mirror upon the knife-edge of a screen K placed in front of and to the side of the photo-electric cell so that when the temperature in the cryostat falls, and the galvanometer mirror is deflected, the image of the lamp filament will move across the knife-edge onto the sensitive plate of the photo-electric cell, whereas when the temperature rises, the image of the lamp filament will cross the

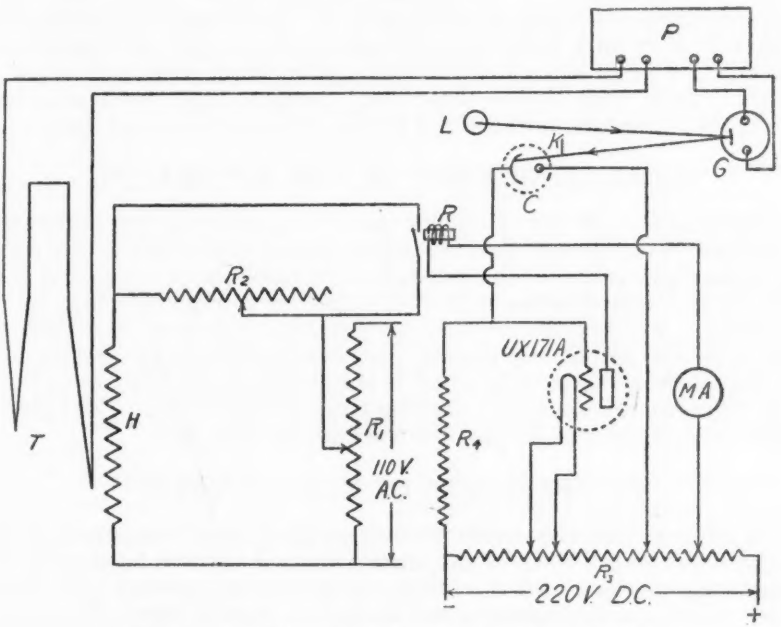

FIGURE 4.—*Diagram of the thermoregulator circuit*

knife-edge onto the screen which will shade the sensitive plate of the cell from the light of the lamp. The photo-electric cell used is of the gas filled, caesium coated plate type. The photo-electric current generated when the light falls on the cell is amplified by means of a single UX No. 171A radio tube, to the grid of which the cathode of the photo-electric cell is connected as shown in the diagram. The various voltages necessary for the photo-electric cell and amplifier are obtained from a slide wire rheostat R_3 of about 400 ohms, equipped with auxiliary sliders, and connected across a 220 volt d. c. supply. The optimum voltages will vary with the cell and amplifier. A potential difference of 135 volts was used in the plate circuit of the amplifier and 70 volts in the photo-electric cell circuit. The grid of the amplifier is given a negative bias of about 30 volts through the resistance

R_4 of 40 megohms which is made up of four 10-megohm grid leaks in series.

In the plate circuit of the amplifier tube is a milliameter (MA) and a 2,000-ohm relay R which opens and closes a shunt circuit around the 50-ohm rheostat R_2 which is connected in series with the heating coil H in the cryostat bath. The voltage applied to this series circuit may be varied from 0 to 110 volts by the rheostat R_1, having a resistance of 400 ohms. The photo-electric cell and amplifier circuit are carefully insulated and the grid leaks and mountings are coated with shellac to make them less affected by humidity. These precautions are necessary for satisfactory operation.

As an alternative to the use of the thermocouple, a coil of platinum wire was used as the thermosensitive element of the regulator by using the coil as one arm of a Wheatstone bridge circuit. The coil, which has a resistance of about 20 ohms at 0° C., was made by winding bare platinum wire on a light frame of mica, and in order to compensate for changes in resistance of the leads, three leads were connected to the coil as is done in the three lead, Siemens type resistance thermometer. For this purpose the bridge ratio should be unity.

III. ARRANGEMENT OF THE APPARATUS

The photograph (fig. 2) shows the arrangement of the apparatus. E is the cryostat proper with the stirrer motor above and to the right. The relay and valve for the constant level mechanism are shown at G. The flask F contains the supply of liquid air to replenish that in the cryostat. The box D contains the galvanometer and photo-electric cell with the amplifying circuit. All the electrical connections lead to the control panel B upon which is mounted also the thermoregulator relay and the resistances controlling the heating current. The potentiometer is shown at C, and the vacuum system at A.

IV. OPERATION OF THE CRYOSTAT

In order to cool the cryostat down to the desired temperature, the space between the walls of the inner Dewar is allowed to come to atmospheric pressure and the falling temperature observed by a platinum resistance thermometer in the bath. Cooling down from room temperature may require from one-half to two hours depending upon the temperature. When the desired temperature is almost reached, the system is evacuated until the temperature is falling very slowly; the temperature now being observed with another galvanometer which can be connected in series with the thermoregulator galvanometer G of Figure 4. The heater resistances are now adjusted until the steady current almost, but not quite, balances the loss of heat from the cryostat. The thermoregulator is started and its operation observed by means of the external galvanometer. Further adjustment of the heating current may be necessary to get the best operation. The difference between maximum and minimum heating current should be just enough to take care of any irregularities of heat conduction into the bath. In order to change to a higher temperature, a heavy current is sent through the heater. A rise in temperature of 20° or 30° may be effected in about 10 minutes.

V. CONSTANCY AND UNIFORMITY OF TEMPERATURE

The external galvanometer also provides an excellent means of determining the temperature variations as the thermoregulator operates. Since the regulator goes through two or three cycles per minute, the temperature oscillations are largely damped in a glass-encased resistance thermometer placed in the bath. However, by observing the deflections of the galvanometer and knowing its sensitivity and the total resistance of the circuit, as well as the thermoelectric power of the thermocouple, the temperature variations may be calculated. It was found that these variations could be made less than 0.001° C. The temperature variations in the bath, using the platinum coil as the thermosensitive element of the regulator, were determined in a similar manner and found to be of about the same magnitude. This constancy and the relatively short period of the regulator indicate that temperature lags and irregularities are very small. In observing the thermoregulator it was noticed that the image of the filament of the lamp L of Figure 4 moves less than a millimeter, corresponding to a change in the electromotive force of the thermocouple of about 0.2 microvolt.

The constancy of temperature over a long period of time depends upon the steadiness of the zero point of the thermoregulator galvanometer, and upon the maintenance of constant current in the potentiometer when the thermocouple is used as the thermosensitive element. A good galvanometer will maintain its zero point very well, so this cause of variation is unimportant. However, there is usually a steady drift in the value of the current through the potentiometer, and this should be made as small as possible by using a good battery as a source of current and insulating this battery against temperature changes. If it is necessary to keep the temperature constant to 0.001° C. for a long time, the potentiometer current or setting should be adjusted occasionally.

When using a resistance as the sensitive element of the regulator, the greatest cause of drift of the thermostating temperature is the change in resistance of the bridge with room temperature. Except when operating near 0° C., the drift is less when using the resistance coil as the thermosensitive element than when using the thermocouple. This comparison was made using manganim resistance coils in the Wheatstone bridge and a lead storage cell as the source of potentiometer current.

In order to test for uniformity of temperature, the bath was explored with a 10-junction copper constantan difference thermocouple. No differences as great as 0.001° C. could be detected in the constant temperature region.

VI. SUMMARY

A cryostat, for use in the temperature range from 0° to −170° C., has been designed and constructed which will automatically maintain a temperature constant and uniform to 0.001° C. Adequate circulation, suitable heat insulation, and a symmetrical distribution of the parts assure great uniformity of temperature. The temperature is maintained constant automatically by a photo-

electric cell thermoregulator. The design is such that it allows for a large unobstructed constant temperature space.

The cryostat is being used for the calibration and standardization of thermometers and for the investigation of the physical properties of materials at low temperatures.

WASHINGTON, January 5, 1931.

THE PAPER-MAKING PROPERTIES OF PHORMIUM TENAX (NEW ZEALAND FLAX)

By Merle B. Shaw, George W. Bicking, and Martin J. O'Leary

ABSTRACT

Experimental tests were made at the bureau to ascertain the suitability of phormium tenax (New Zealand flax) fiber for paper manufacture.

Phormium tenax is a plant of the lily family native to New Zealand, where it grows luxuriantly under a wide range of conditions. It is cultivated to only a limited extent, but reports state that if the demand warranted it would be produced on a large scale, sufficient for commercial consideration for paper making. At present it is used principally for cordage, but it does not withstand well the alternations of wetness and dryness to which rope is frequently subjected, and therefore has not competed very successfully with other cordage materials.

Three representative samples—unscutched, scutched, and tow—were employed in the tests. Experimental papers were made on both laboratory and semicommercial scale.

In a number of the tests the preparation of the pulp included two successive cooking operations, fractional digestion. Either the caustic-soda process or the 2-stage cooks using sodium sulphite and caustic soda, respectively, gave very good results, on the basis of both quality of fiber produced and yield obtained.

The tests indicate that phormium is a promising material for the manufacture of wrapping or writing papers, but that the fiber must be thoroughly cleaned mechanically before being submitted to the paper-making processes. The scutched material showed the best possibilities.

Data are given relative to the kind and amount of chemicals used in the cooking liquor, yield of unbleached pulp, bleaching quality of the pulp, and physical and chemical properties of the papers made.

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I. INTRODUCTION

Experimental paper-making tests have recently been made at the National Bureau of Standards to ascertain the suitability of phormium tenax (New Zealand flax) fiber for paper manufacture. The tests were

made in cooperation with the New Zealand department of scientific and industrial research. The increasing consumption of pulp and paper products and the gradual diminution of the supply of raw materials commonly used in their manufacture make such potential sources of paper-making fiber of considerable interest. The data obtained, together with comments and discussion, are, therefore, reported here for the general information of the paper industry.

II. OCCURRENCE AND CHARACTERISTICS

1. GENERAL [1]

Phormium fiber is obtained from the leaves of phormium tenax, a native plant of New Zealand. It was for a long time commonly known in the market as New Zealand flax. The term is misleading, however—flax belonging to the *Linaceæ* family, phormium to the *Liliaceæ*—therefore the correct name, phormium, is now more generally applied.

Phormium tenax growing under virgin conditions has a range in altitude from sea level to perhaps 4,000 feet. It is distributed in both swamps and hillsides, but light rich soil by the side of rivers and brooks is best suited to its cultivation as a commercial crop. It is propagated from seeds or from division of the rootstock.

The plant has no upright stem. A creeping stem, or rootstock, spreads horizontally beneath the surface of the soil, and from it grow narrow, sword-shaped leaves, from 2 to 4 inches wide and from 4 to 8 feet long, arranged in fan-shaped clusters similar to those of the iris or garden flag. (See fig. 1.)

Considered with reference to the portion of the plant from which they are derived, vegetable fibers may be classed as seed fibers (such as cotton) growing from the seeds of the plant, stem fibers (such as flax, jute, and ramie) growing in the bast of dicotyledonous plants, and leaf fibers (which include manila, sisal, and phormium) occurring in the leaf tissues of monocotyledonous plants.

Although stem fibers are known commercially as soft fibers and leaf fibers as hard, phormium is rather soft, and with extra care in preparation may be spun and woven into cloth resembling linen duck. Its principal use is for cordage at the present time, however, either alone or in combination with manila, which it resembles in appearance. It is said to be suitable for binder twine, but it does not withstand well the alternations of wetness and dryness to which ropes are frequently subjected and, therefore, has not competed very successfully with other cordage materials.

In the normal preparation of the fiber the leaves are fed into a stripping machine which beats off the bulk of the green nonfibrous tissue, and the fiber is passed to the washing machines where most of the loose vegetable matter remaining is washed away. The washed fiber is formed into hanks and hung over poles outdoors to dry and to be bleached by exposure to the weather. The dried material at this stage constitutes the commercial unscutched fiber.

If the fiber is to be further refined it is next scutched to remove any dry vegetation adhering. The short, broken fiber separated in the scutching process is recovered and is marketed as tow.

[1] The botanical information was obtained from New Zealand department of agriculture Bulletin No. 95, Phormium tenax, by E. H. Atkinson; 1922. The economic data were supplied by E. Marsden, secretary, New Zealand department of scientific and industrial research.

FIGURE 1.—*A phormium tenax plant*

UNIV OF MICH

In order to be of commercial value for paper making, fiber must not only be suitable for such use, but also be available in large quantity, more or less constant, and at a low cost. At present approximately only 25,000 tons of phormium are exported annually, and the cost of the fiber prepared for cordage manufacture is about $100 per ton; but reports state that if the demand warranted the plant could be cultivated on a large scale, sufficient for commercial consideration, and that the present cost of production, which is now chiefly labor costs, would be very considerably reduced, since mechanical harvesters and conveyors and improved methods of refining would then be worth while.

2. TEST SAMPLES

Three different samples of phormium were employed in the paper-making tests. The samples were designated as unscutched, scutched, and tow, and were representative of the fiber at the corresponding stages of preparation. The material was supplied by the New Zealand department of scientific and industrial research.

III. PAPER-MAKING EQUIPMENT

The tests were made on both laboratory and semicommercial scale. The laboratory equipment used in the preparation of the pulp and its subsequent conversion into paper consisted of a small rotary boiler, one-half pound beater (capacity one-half pound of dry fiber), fiber-sheet mold, sheet press, and sheet dryer. The equipment is used at the bureau for the laboratory paper-making tests of all materials under investigation and has been fully described and illustrated in previous bureau publications.[2]

The equipment of the bureau paper mill is adapted for making paper on a semicommercial scale under practical mill conditions. The equipment employed in the phormium tests was that in general use in the mill and consisted of a rag duster; rag cutter; rotary boiler; 50-pound copper-lined wood-tub beater, having manganese-bronze bars and plate, and equipped with a washing cylinder; Jordan refiner, with bars of a bronze and steel alloy; 4-plate screen; and 29-inch Fourdrinier paper-making machine, with wire 33 feet long and having two presses, nine 15-inch dryers, a small machine stack of seven rolls, and a reel.[3]

IV. EXPERIMENTAL PROCEDURE AND DATA

1. COOKING CONSTANTS

The kinds and amounts of chemical solvents employed in the boiling solutions to dissolve the noncellulose material and soften the paper-making fiber are shown in Table 1. As will be noted, in a number of the tests the phormium was cooked twice, fractionally digested, the spent liquor from the first digestion being drained off

[2] Merle B. Shaw, George W. Bicking, and Leo W. Snyder, The Preparation of Fiber Test Sheets, Paper Trade J., **90**, No. 16, pp. 60-66; Apr. 17, 1930; also, B. S. Jour. Research, **5**, pp. 105-114; July, 1930. Merle B. Shaw, Equipment and Research of the Bureau of Standards Paper Mill, Paper Trade J., **89**, No. 19, pp. 60-63; Nov. 7, 1929.

[3] Photographs of equipment are shown in B. S. Tech. Paper No. 340, Caroá Fiber as a Paper-Making Material, pp. 338-341; also Equipment and Research Work of the Bureau of Standards Paper Mill, Paper Trade J., **89**, No. 19, pp. 60-63; Nov. 7, 1929.

after the completion of that operation and fresh solution being added for the next. The constant factors were in general as follows:

Laboratory:		
Weight of bone-dry material	pounds	1½
Volume of water	liters	8
Cooking temperature	°F	340–345
Cooking pressure	pounds per square inch	120
Time for raising to cooking temperature	hour	1
Duration of cooking temperature	hours	4
Time for cooling	hour	½
Semicommercial:		
Weight of bone-dry fiber	pounds	80
Volume of water	gallons	60
Cooking temperature	°F	290–300
Cooking pressure	pounds per square inch	70–80
Time for raising to cooking temperature	hour	1
Duration of cooking temperature	hours	6

2. PAPER MAKING

The table gives data relative to the stage of refinement of the phormium when received (scutched, unscutched, or tow), chemicals used in the cooking liquor, yield of unbleached pulp, bleaching quality of the pulp, and measurements on the physical and chemical properties of the papers made. The percentage of chemical used in cooking is based on the bone-dry weight of the fiber furnished to the boiler; the yield of pulp is on the air-dry basis. Bleaching tests were made on samples of most of the pulps. The quantity of bleaching powder employed is expressed in terms of the bone-dry weight of the cooked and washed fiber. The laboratory sheets were made from unbleached pulp; whereas with two exceptions—runs Nos. 809 and 810—the semicommercial runs were on bleached stock. Further description of the individual tests follows.

TABLE 1.—*Measurements on papers made from phormium*

A. LABORATORY TESTS

Test identification No.	Condition of raw fiber	Cooking chemicals				Yield of unbleached pulp (air-dry basis)	Bleaching powder required to bleach pulp [2]	Pulp used for paper, bleached or unbleached	Physical tests on finished paper [1]			
		First cooking [1]		Second cooking [1]					Weight, 500 sheets 25 by 40 inches	Bursting strength	Ratio of bursting strength to weight (500sheets 25 by 40 inches)	Thickness
		Kind	Amount	Kind	Amount							
			Per cent		*Per cent*	*Per cent*	*Per cent*		*Pounds*	*Points*	*Per cent*	*Inch*
Cook No. 54	Unscutched	Lime	10	Soda ash	25	69.4						
Cook No. 62	do	Sodium sulphite	25	Caustic soda	10	37.2	10–12	Unbleached	55.6	50.4	90.5	0.0048
Cook No. 55	Scutched	Caustic soda	25			57.2	14–16	do	52.6	70.6	127.0	.0040
Cook No. 56	do	do	10	Caustic soda	15	52.3	12–14	do	56.9	49.3	86.6	.0041
Cook No. 57	do	Sodium sulphide Caustic soda	10 15			62.2		do	58.1	66.9	115.0	.0048
Cook No. 58	do	Sodium sulphite	25			63.0		do	54.6	71.1	130.0	.0041
Cook No. 59	do	Bleaching powder	10	Caustic soda	25	50.0	16	do	55.2	43.8	79.0	.0048
Cook No. 61	do	Sodium sulphite	25	do	10	48.5	10–12	do	56.6	60.7	107.0	.0042
Cook No. 65	do	Caustic soda	10	Sodium sulphite	25	51.5						

B. SEMICOMMERCIAL TESTS

Run No. 808	Unscutched	Caustic soda	25			57.2	20	Bleached	56.8	37.7	66.4	.0039
Run No. 809	do	do	25			57.2		Unbleached	58.9	61.6	104.5	.0041
Run No. 810	do	do	10			78.6		do	57.5	52.5	91.3	.0046
Run No. 813	Scutched	Sodium sulphite	25	Caustic soda	10	51.0	12–14	Bleached	56.1	40.1	71.5	.0040
Run No. 816	Tow	Caustic soda	25			51.5	12–16	do	55.1	42.6	77.3	.0034

[1] Most of the cooks were 2 stage, the pulp being drained before the second cooking.
[2] Bleaching powder contained 35 per cent of available chlorine.
[3] See foot note 3, p. 416.

TABLE 1.—*Measurements on papers made from phormium*—Continued

A. LABORATORY TESTS—Continued

Test identification No.	Physical tests on finished paper—Continued [1]								Chemical tests		
	Tensile strength (strip 15 by 100 mm)		Elongation (strip 15 by 100 mm)		Tearing strength		Folding endurance		Ash	Alpha [2] cellulose	Copper [3] number
	Machine direction	Across machine direction	Machine direction	Across machine direction	Machine direction	Across machine direction	Machine direction	Across machine direction			
	kg	*kg*	*Per cent*	*Per cent*	*g*	*g*	*Double folds*	*Double folds*	*Per cent*	*Per cent*	
Cook No. 62	7.1	6.9	5.5	5.1	109.6	104.2	1,125	1,290	0.55		
Cook No. 55	10.2	10.0	6.2	6.1	84.2	86.4	3,430	3,400	.95		
Cook No. 56	7.4	7.5	6.4	6.4	76.8	71.4	1,205	1,215	.54		
Cook No. 57	9.1	9.4	6.0	6.3	152.6	165.4	3,445	3,325	1.10		
Cook No. 58	10.3	10.7	6.2	5.9	170.8	150.4	4,000	3,160	.56		
Cook No. 59	6.7	6.7	4.9	4.2	74.4	67.0	555	540	2.28		
Cook No. 61	8.5	8.7	6.4	6.1	122.4	98.4	3,150	2,810	.50		

B. SEMICOMMERCIAL TESTS—Continued

Run No. 808	9.1	6.2	2.2	6.6	64.4	63.4	341	487	.98	67.5	5.158
Run No. 809	11.9	7.9	3.3	10.0	106.6	98.4	4,060	2,824	1.13	82.1	.575
Run No. 810	10.8	6.5	3.2	9.9	114.0	95.2	1,510	2,250	.85		
Run No. 813	9.2	6.0	2.8	8.8	63.8	67.6	670	1,305	.90	73.4	2.888
Run No. 816	9.6	5.7	2.6	10.2	71.2	78.0	536	864	1.30	70.8	3.648

[1] Methods employed in making the measurements are fully described in Paper Testing Methods, published by the Technical Association of the Pulp and Paper Industry, 18 East Forty-first Street, New York, N. Y.

[2] The method used to determine alpha cellulose is described in Bureau of Standards Research Paper No. 107, A Study of Purified Wood Fibers as a Paper-Making Material, by Royal H. Rasch.

[3] The method now used at the bureau will appear in a later publication.

(a) LABORATORY

(1) *Unscutched fiber.*—Paper-making pulp was prepared from the unscutched phormium by two successive cooking operations. As previously stated, after completion of the first stage of the cooks, the liquor was drained off, the fresh solution was added, and the operation was continued. Cook No. 54 was with 10 per cent of lime and 25 per cent of soda ash, respectively. The resultant pulp was raw and appeared not to have received drastic enough chemical treatment. A small beater of stock was prepared from it, however, and made into sheets, but the paper was not sufficiently satisfactory to justify making the physical and chemical tests.

For cook No. 62 the phormium was first threshed and dusted. The fiber loss in these operations was approximately 10 per cent. The cooking chemicals were sodium sulphite and caustic soda. The yield of pulp was 41.3 per cent, based on the weight of fiber furnished to the boiler, or 37.2 per cent if expressed in terms of the weight of the phormium before it was threshed or dusted.

(2) *Scutched fiber.*—Cooks Nos. 55 and 56 were both with 25 per cent of caustic soda, but for No. 56, 10 per cent was used first and the cooking repeated with 15 per cent. The pulps bleached satisfactorily and the fibers were fairly clean. Neither the pulp nor the finished paper for cook No. 56 seemed any better, however, than for cook No. 55.

The cooking solution for No. 57 was a mixture of sodium sulphide and caustic soda. The pulp could not be bleached satisfactorily, and the paper made was, therefore, suitable only for wrapping or similar uses. Perhaps, the amount of caustic soda added should not have been decreased—should have been 25 per cent, as in cook No. 55—but the results obtained were not sufficiently promising to warrant making such a cook.

For the next cook (No. 58), 25 per cent of sodium sulphite was used. The resultant pulp did not bleach satisfactorily on account of the presence of unreduced woody sections, but it was the cleanest and the best in color of any of the pulps thus far obtained. The papers made from this cook and from No. 57 were somewhat leathery in appearance. As shown in the table, they were high in tearing resistance, and had good folding endurance. Possibly part of the resins, gums, pectins, etc., were not removed in the boiling and acted as binding or cementing material.

The phormium of cook No. 59 was first treated with 10 per cent of bleaching powder. At this stage the fiber was warmed, but was not raised to the temperature of the other cooks. The cooking constants were followed otherwise. It was thought that perhaps the lignin would be resolved by the bleach, and consequently a cleaner and better pulp would be obtained in the subsequent caustic-soda process; but the pulp did not bleach as well as that of cook No. 55, in which caustic soda only was used. The color of the bleached fiber was dead, not bright as the other pulps had been. The reaction of the lime in the bleach liquor with the lignin may have formed products which were insoluble in the caustic soda solution and, therefore, not removed in the second cook. Treating the phormium with chlorine gas instead of bleaching liquor before boiling it with caustic soda

might be more satisfactory; but since the cooks that were made with sodium sulphite showed the most promising results, it was thought that any additional tests should be concentrated along that line. The strength of the paper made was less than that from the other cooks. The high ash content was doubtless due to lime from the bleaching treatment.

The next cook (No. 61) was first made with 25 per cent of sodium sulphite and then with 10 per cent of caustic soda (16 per cent if based on the approximate weight of the pulp after the sulphite cooking). The pulp was very clean, and the paper made from the unbleached stock was of good quality.

When sodium sulphite was used in the previous fractional digestions, it was used in the first stage. The order was reversed in cook No. 65. The yield of pulp by this latter procedure compared favorably with that obtained in the other cooks, but the color of the unbleached pulp was not nearly so good.

Following the completion of the other laboratory and the semicommercial tests, supplementary tests were made using a treatment with weak alkali at comparatively low temperature as the first stage of the fractional digestion.

W. Raitt, of the Forest Research Institute, Dehra Dun, India, has for several years been working on an inexpensive and satisfactory method for converting bamboo into a good pulp. In order to whiten the pulp obtained by the usual cooking methods, a large amount of bleach was necessary. Raitt found during the course of his experiments that by first treating the bamboo with a weak alkali solution at comparatively low temperatures and then with stronger caustic at higher temperatures most of the bleaching difficulties were overcome. He discovered that the trouble was not inherent in the fiber or the incrusting lignin, but was in the type of pectin present. He found that pectins are easily soluble at the lower temperature, but that the transformation products combine with soda at the higher temperatures to produce a dark brown solution of great staining power, which is absorbed by the cellulose in the digester and requires for removal bleaching so severe as to be destructive of fiber.[4]

The method used by Raitt was believed to be equally well suited to other grasses and was that applied in the supplementary tests on phormium.

To extract and eliminate the starch and pectuous constituents before the phormium was broken down into fiber; that is, before the lignin was removed, the phormium was first treated with a weak solution of caustic soda, 0.85 per cent (10 per cent if based on weight of phormium), at 200° to 210° F. This digestion was followed by boiling with a solution of 2½ per cent (30 per cent if based on original weight) caustic soda at 340° F. The pulp produced was less deeply stained and bleached with approximately 10 per cent of bleaching powder, but the final product differed little from that obtained by fractional digestion with sodium sulphite and caustic soda.

[4] W. Raitt, The Bamboo Hope, Procs. Technical Section, Papermakers' Association of Great Britain and Ireland, pp. 89–101; October, 1927. Abstracted in Paper Trade J., **85**, No. 16, pp. 48–50; Oct. 20, 1927. The Fractional Digestion of Bamboo and other Grasses Producing Annual Culms, pp. 331–341 of Modern Paper Making, by Clapperton and Henderson, 1929; Ernest Benn (Ltd.), Bouverie House, Fleet Street, E. C. 4, London.

FIGURE 2.—*Phormium tenax fiber.* × 100

(b) SEMICOMMERCIAL

(1) *Unscutched fiber.*—A cook was made with 25 per cent of caustic soda. One-half of the resultant pulp was washed, bleached, and converted into paper in run No. 808. The stock on the paper machine was "slow," but caused no trouble. When leaving the presses the paper seemed to be very tough and strong, but after going over the dryers it was somewhat brittle and had lost much of its strength. Apparently the nonfibrous constituents were not all removed in the cooking, washing, and bleaching operations, and when subjected to the heat of the dryers made the paper brittle. Viewed in the microscope the fibers of the stock looked very clean, but evidently they needed to be purified more.

Run No. 809 was on the remaining half of the cook, but the pulp was not bleached. As for run No. 808, the paper appeared promising when leaving the presses but lost strength and became brittle when dried.

Run No. 810 was wrapping paper, unbleached. The stock did not screen satisfactorily through screen plates with either 0.024 or 0.036 inch slots. Apparently the nonfibrous materials not removed in the cooking were the cause of the difficulty. The stock was finally run out without being screened. The loss of strength of the paper in drying described in the preceding runs was also experienced here.

(2) *Scutched fiber.*—For the scutched fiber sodium sulphite was used in the first digestion stage and caustic soda in the second. No trouble was experienced in the run and the resultant paper was of good quality.

(3) *Tow.*—Run No. 816 was with tow, the coarse and broken part of the phormium separated in the process of cleaning, cooked with 25 per cent of caustic soda.

The chemical test data reported in the table were not available at the time the paper runs were being made, therefore several changes that it is now evident should have been made were not included. The low alpha cellulose content indicates that the purification of the pulp was insufficient. The high copper numbers indicate that the pulps were overbleached, or, perhaps, that impurities not eliminated in the cooking and washing processes reacted with the bleach, and that the resultant products were not removed in the subsequent washing operation. At the time run No. 808 was made the pulp was believed to be overbleached.

3. FIBER MEASUREMENTS

Figure 2 is a photomicrograph [5] of unbleached scutched phormium fiber. The figure shows the fibers to be long and narrow with pointed ends, somewhat like linen in appearance, but more smooth and without markings.

The length of the fiber varies from 1.63 to 4.37 mm, and the diameter from 0.006 to 0.020 mm. The following fiber measurements afford comparison of phormium with other paper-making fibers.

[5] Photomicrograph and phormium fiber measurements were made by Mary L. Rollins, of this bureau; dimensions of other fibers were taken from standard textbooks.

Fiber	Length	Diameter	Ratio of length to diameter
	mm	*mm*	
Cotton	20–50	0.012–0.037	1,400:1
Flax	25–30	1.02	1,200:1
Manila hemp	[1] 6	1.024	250:1
Jute	[1] 2	1.022	90:1
Spruce wood	[1] 2.8	1.033	90:1
Phormium tenax	[1] 2.7	1.014	190:1

[1] Average.

V. CONCLUSIONS

From the results obtained in the tests it is apparent that phormium needs to be thoroughly cleaned mechanically before being submitted to paper-making processes. The scutched material, that from which the greatest amount of the nonfibrous tissue has been removed previous to being marketed, has the best possibilities. Additional mechanical cleaning is required in the paper mill, however, preparatory to the pulping operation. A method suggested is that the phormium be passed through a machine to loosen it; placed upon conveyors of wire screening, for sorters to pick out weeds, roots, dead plants, etc., that may have escaped removal at time of preparation; and dusted to remove all remaining fine foreign material, such as fruit seeds, sand, etc., before being cut into desired lengths for boiling.

The best digestion procedure depends somewhat upon mill conditions. In the work at the bureau either the caustic soda process or the two-stage cooks using sodium sulphite and caustic soda, respectively, gave very good results, on the basis of both quality of fiber produced and yield obtained. No special equipment is required for the caustic-soda process; whereas when sodium sulphite is employed, the boiler should be of an acid-resistant material. An ordinary iron rotary boiler was used at the bureau, but considerable trouble was caused by iron rust from the sodium sulphite digestion. The process is believed to be very promising, however.

The experimental tests indicate that phormium is a promising material for the manufacture of wrapping or writing papers.

WASHINGTON, January 13, 1931.

A METHOD FOR THE SEPARATION AND GRAVIMETRIC DETERMINATION OF OSMIUM

By Raleigh Gilchrist

ABSTRACT

A procedure for the separation and gravimetric determination of osmium is described. This procedure involves the separation of osmium from other metals by distillation as the volatile tetroxide and its recovery from solution by hydrolytic precipitation. A very suitable reagent for the quantitative absorption of the distilled tetroxide was found to be 6 normal hydrochloric acid saturated with sulphur dioxide. The recovery of osmium was accomplished by precipitating the hydrated dioxide from a boiling solution at acidities ranging from pH 1.5 to 6.3, after sulphite compounds had been decomposed by repeated evaporation with hydrochloric acid. The hydrated dioxide was impregnated with ammonium chloride to prevent mechanical loss when ignited to metal under hydrogen.

The thiourea test devised by Chugaev for the detection of small quantities of osmium was modified so that it could be applied to solutions containing nitric acid. The test was found to be sensitive to 1 part in 5,000,000 parts of solution, which is 50 times as sensitive as stated by Chugaev.

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I. INTRODUCTION

The most outstanding property of osmium is the formation of a volatile oxide of the composition OsO_4. This oxide is produced when solutions of osmium are treated with oxidizing reagents or when solutions containing compounds of osmium decompose under certain conditions. It is also produced when osmium is heated in an atmosphere either of air or of oxygen and even when osmium sponge is allowed to remain in contact with air at room temperature. It might well be said that the chemistry of osmium revolves about this oxide, since any work with this element is almost certain to involve at some stage the formation of the tetroxide.

The ready formation of the tetroxide of osmium is made use of in separating osmium from the other platinum metals, not only for purposes of refining, but also for purposes of analysis. The tetroxide melts at about 40° C.,[1] [2] boils at 129° C.[2] and can be distilled from aqueous solution. According to Deville and Debray,[3] who determined the vapor density of osmium tetroxide, the compound is stable at temperatures up to 285° C. More recently, von Wartenberg[4] found that the tetroxide is not decomposed at temperatures up to 1,500° C.

While the vapor of osmium tetroxide shows an astounding degree of stability when pure or in the presence of oxygen, it is extremely unstable if reducing substances, such as alcohol, formaldehyde, hydrazine, etc., are present. Reduction, however, usually goes only to the dioxide[5] and not to the metal.

Thus the tendency of osmium to form tetroxide, which may escape, introduces difficulties into the quantitative handling of the element, while the readiness with which the tetroxide suffers reduction in the presence of organic matter further complicates the transfer of osmium tetroxide by distillation. For instance, the apparatus used must be constructed wholly of glass and no organic lubricant can be used on ground joints.

The method employed for the determination of the osmium content of a material will depend to a great extent upon the nature of the material. In many of the pure compounds of osmium, such as ammonium chloroosmate $(NH_4)_2OsCl_6$, ammonium bromoosmate $(NH_4)_2\ OsBr_6$, etc., the determination can be made simply by heating the substance in an atmosphere of hydrogen. The resulting product, which will consist only of metallic osmium, is then weighed. If the compound be potassium chloroosmate (K_2OsCl_6), potassium bromoosmate (K_2OsBr_6), etc., it becomes necessary, in addition, to remove the soluble alkali salt from the resulting osmium sponge by leaching with water.

Such methods as those just mentioned are of little use, however, when the osmium is present in solution with other metallic elements or combined in such materials as crude platinum, osmiridium, etc. It then becomes necessary to make first a separation of the osmium from the elements which accompany it. This separation is usually

[1] F. Krauss and D. Wilken, Z. anorg. allgem. Chem., **145**, p. 151; 1925.
[2] H. von Wartenberg, Ann., **440**, p. 97; 1924.
[3] H. Ste-C. Deville and H. Debray, Ann. des Mines, (5) **16**, p. 22; 1859. Encyclopédie Chimique, 30 (1), p. 73.
[4] See footnote 2.
[5] C. Paal and C. Amberger, Ber., **40**, p. 1378; 1907.

accomplished by the formation of osmium tetroxide, which is distilled from solution and recovered by absorption in some reagent.

A number of gravimetric methods have been investigated for the removal of osmium from the absorbent solutions and for the conversion of the precipitate to a weighable form. A survey of these methods shows that, in nearly every case, the precipitate which is removed from the absorbent solution consists of hydrated osmium dioxide, and that the difference in the methods is merely the manner in which the precipitate is obtained and subsequently treated. In addition to gravimetric methods, at least one volumetric procedure has been proposed, in which the osmium as tetroxide is reduced to quadrivalent osmium, liberating free iodine, which is titrated with a solution of sodium thiosulphate.

Paal and Amberger [6] made a notable contribution by studying not only the gravimetric methods known at the time, but also by investigating various other possible analytical procedures. Although the results obtained by these authors are described in detail in the reference mentioned, a brief description of their methods and results may help to make clear the difficulties encountered in the determination of osmium.

1. A procedure which involved the separation of osmium from alkaline osmate solutions in the form of Frémy's salt, osmyl tetrammine chloride, $OsO_2(NH_3)_4Cl_2$, by precipitation with ammonium chloride in a solution of hydrochloric acid, and subsequent reduction of the compound obtained to metal [7] in hydrogen, gave recoveries of osmium which varied considerably and were roughly 10 per cent short of the quantities of osmium taken. This procedure was rejected by Paal and Amberger as unusable.

2. The method of Leidié and Quennessen [8] which consisted of the precipitation of metallic osmium from alkaline solutions of sodium osmate by aluminum, was found to give incomplete precipitation of osmium. Furthermore the precipitate was contaminated by compounds of aluminum. It was found that the precipitate produced was not metallic osmium, as thought by Leidié and Quennessen, but osmium dioxide. The results obtained by the method were too low to establish it as a usable procedure.

3. A statement by Frémy [9] that osmium disulphide was precipitated from solutions of potassium osmate (K_2OsO_4), by hydrogen sulphide, led Paal and Amberger to consider this reaction as a possible means of recovering osmium from solutions of osmium tetroxide in sodium or potassium hydroxide to which alcohol has been added. The alkaline solution was treated with hydrogen sulphide, then made acid with dilute sulphuric acid and again saturated with hydrogen sulphide. The precipitate obtained was found not to be the disulphide, but a hydrated oxysulphide of similar composition to that obtained by von Meyer [10] by the action of hydrogen sulphide on osmium tetroxide. Von Meyer stated that he was able to obtain osmium free from sulphur by igniting this precipitate in hydrogen, a goal which Paal and Amberger were unable to attain. At times osmium was found to be present in the filtrates and in the wash

[6] See footnote 5, p. 422.
[7] A. Classen, Ausgewählte Methoden der analyt. Chem., **1**, p. 277; 1901.
[8] E. Leidié and L. Quennessen, Bull. Soc. Chim. (3), **29**, p. 805; 1903.
[9] E. Frémy, Ann. chim. phys. (3), **12**, p. 521; 1844.
[10] E. von Meyer, J. prakt. Chem. (2), **16**, p. 77; 1877.

waters. The recoveries varied widely, being sometimes greater than the quantities of osmium taken, so that determinations based upon this procedure were unreliable.

4. The use of hydrazine hydrate in the production of colloidal osmium preparations from alkaline osmate solutions was extended by Paal and Amberger in order to determine whether this reagent could be used to precipitate osmium for analytical purposes. The filtrates were found to contain considerable quantities of osmium while the precipitates which were obtained were very difficult to filter. When applied to solutions of osmium tetroxide in alcohol, diluted somewhat with water, hydrazine hydrate caused reduction to commence immediately, but the precipitation did not always behave in the same manner under apparently similar conditions. Warming the solution appeared to hasten the precipitation while the presence of ammonium chloride hindered it. The precipitate obtained was not osmium, but again the hydrated dioxide.

5. Another possibility which Paal and Amberger considered was the absorption of osmium tetroxide in a solution of ammonium hydroxide and ammonium chloride, evaporation of the resulting solution to dryness on the steam bath, and the reduction of the residue to metal in hydrogen. The average value found in three experiments was about 1.5 per cent less than the quantity of osmium taken. The authors considered that this method gave too low results.

6. Two other possibilities, which consisted in the treatment of solutions of osmium tetroxide in alcohol by formaldehyde and by the acetaldehyde produced by the action of sunlight, gave precipitates of hydrated dioxide and results which were low by about 0.4 to 0.6 per cent. Difficulty was encountered in the coagulation, settling, and filtration of the precipitates obtained, the filtration taking from one to two days.

7. Included in this series of studies was a volumetric method of Klobbie[11] based on the reaction of osmium tetroxide with potassium iodide in acid solution. The iodine liberated by the reduction of osmium tetroxide to quadrivalent osmium was titrated with $N/100$ sodium thiosulphate. Experiment showed that for more concentrated solutions the results varied widely and only from 83 to 95 per cent of the osmium tetroxide taken was found. Paal and Amberger concluded that this method was apparently applicable only to very dilute solutions.

8. As a result of their investigations Paal and Amberger developed a method which they considered gave them the best results. According to the observations of Frémy[12] and of Claus,[13] pure osmate solutions decompose on acidification with the formation of osmium dioxide and of osmium tetroxide. Moraht and Wischin[14] found that if alcohol is present the osmium is precipitated from solution as a finely divided hydrated oxide which could be obtained free from alkali only by washing with water for a number of days. Paal and Amberger's procedure consisted in the conversion of osmium tetroxide, in a solution of potassium hydroxide and alcohol, into potassium

[11] E. A. Klobbie, Chem. Zentralbl., **2**, p. 65; 1898.
[12] Frémy, J. prakt. Chem. (1), **33**, p. 407; 1844; (1), **34**, p. 308; 1845.
[13] C. Claus, J. prakt. Chem. (1), **34**, p. 420; 1845.
[14] H. Moraht and C. Wischin, Z. anorg. Chem., **3**, p. 153; 1893.

osmate, K_2OsO_4, by heating the solution at 40° to 50° C. An excess of alcohol was kept present in order to reduce any osmium tetroxide which was formed. The solution was acidified with dilute sulphuric acid, in slight excess, and allowed to remain for 10 to 12 hours. The black precipitate which settled out was separated from the colorless mother liquor by filtering through a tube having an asbestos pad. The precipitate was washed with a solution of water and alcohol until sulphuric acid was eliminated, drained as dry as possible by suction, and placed in a desiccator over caustic soda. In order to prevent the formation of tetroxide, alcohol vapor was kept in the desiccator. The precipitate was reduced to metal by carefully heating it in hydrogen, the apparatus having been first freed from air by carbon dioxide. The average result of three experiments showed that recovery of the osmium was about 0.25 per cent less than the quantity taken.

1. METHOD OF RUFF AND BORNEMANN

Ruff and Bornemann[15] modified the method of Paal and Amberger as a result of the observation that the formation of a colloidal solution was wholly avoided if care were taken to establish complete neutrality of the alkaline osmate solution while it was heated on the steam bath. In the hands of Ruff and Bornemann, the method of Paal and Amberger was adapted to the analysis of chloride and of fluoride compounds of osmium as follows:

The chloride or fluoride was dissolved in a solution of caustic alkali containing alcohol and heated on the water bath either in a platinum dish or in a beaker of resistance glass. The excess of alkali was neutralized, while the solution was hot, with either 2 normal sulphuric acid or with hydrochloric acid, using phenolphthalein as indicator, and the solution allowed to stand on the water bath. Additional acid was added from time to time to discharge the recurring pink color of the indicator. When the hydrated osmium dioxide settled out, leaving the mother liquor colorless, the reaction was regarded as complete. Since the hydrated dioxide so obtained could not be heated at temperatures from 100° to 150° C. without undergoing explosive decomposition, Ruff and Bornemann attempted to diminish this tendency to deflagrate by allowing the precipitate and solution to remain on the water bath an additional six hours. They found also that the precipitate was difficult to filter and to wash. The precipitate was dried by gradually heating it to 150° C. in a current of carbon dioxide laden with alcohol vapor, then in a current of pure carbon dioxide to 250° C., and weighed as anhydrous osmium dioxide, OsO_2. A supplementary determination was made by then igniting the anhydrous dioxide to metal in hydrogen.

This procedure of Paal and Amberger, modified in some details by Ruff and Bornemann, is undoubtedly the best of the published methods for the determination of osmium. There are a number of features about it, however, which make it troublesome to use. For instance, if glass beakers are employed the precipitate is contaminated by silica which has been dissolved by the hot alkaline solution. A correction for the silica can be made only by igniting the metallic residue in air or in oxygen, the osmium being then either lost or

[15] O. Ruff and F. Bornemann, Z. anorg. Chem., **65**, p. 429; 1910.

requiring the additional trouble of subsequent recovery. The time required to prepare the precipitate for filtration is far too great, and hydrated oxides produced from alkaline solutions appear to have considerable tendency to become colloidal during washing. Howe and Mercer[16] found this to be the case with hydrated ruthenium oxide hydrolyzed from alkaline solutions. Furthermore, there appears to be a tendency for such precipitates to retain alkali, probably by adsorption, so that even long continued washing may not always be effective. Perhaps the chief difficulty in the method and the one which requires care, patience, and cumbersome apparatus to overcome is the conversion of the hydrated dioxide to metal. Both Paal and Amberger, and Ruff and Bornemann found that the hydrated dioxide of osmium deflagrated on heating, and elaborate precautions were taken to avoid the consequent mechanical loss of osmium. These investigators attributed the phenomenon to the removal of water from the hydrated compound. Deville and Stas[17] observed the same behavior in the ignition of hydrated iridium dioxide, while in earlier work[18] in this laboratory it was found that the most difficult step in the development of a gravimetric method for the determination of ruthenium was eliminating the tendency of the hydrated oxide to deflagrate when it was ignited to the anhydrous oxide.

2. METHOD OF OGBURN AND MILLER

In a recent article by Ogburn and Miller[19] a method was proposed for the determination of osmium, using strychnine sulphate as a precipitating reagent. The authors state that when a saturated solution of strychnine sulphate is added to a slightly acidified solution of sodium chloroosmate (Na_2OsCl_6) the osmium is completely precipitated as a heavy canary yellow compound and that no osmium can be detected in the supernatant liquor by hydrogen sulphide or by thiourea. They state further that the compound contains neither chlorine nor the sulphate radical, and that it is probably composed of one atom of osmium combined with three strychnine radicals, $(C_{21}H_{22}O_2N_2)_3Os$. However, in determining osmium by drying and weighing the precipitate, the empirically determined factor 0.1758 was used. No explanation is given for the discrepancy between this factor and that calculated from the postulated formula, which is 0.1599.

The writer made a number of trials of the method of Ogburn and Miller, in which their directions were carefully followed, except that larger quantities of osmium were taken, to minimize errors of weighing, etc., and with the further exception that weighed portions of ammonium chloroosmate and of ammonium bromoosmate, of known osmium content, were used instead of the solution of sodium chloroosmate used by Ogburn and Miller. It was found that the filtrates invariably contained osmium, apparently because some solution of the precipitate occurred during washing. Furthermore, the precipitate formed by adding strychnine sulphate to the solution of chloroosmate was not identical with that formed from the bromoos-

[16] Jas. L. Howe and F. N. Mercer, J. Am. Chem. Soc., **47**, p. 2926; 1925.
[17] H. Ste-C. Deville and J. S. Stas, Procès-verbaux, Comité International des poids et mesures, p. 195; 1877.
[18] R. Gilchrist, B. S. Jour. Research, **3**, p. 993; 1929.
[19] S. C. Ogburn, jr. and L. F. Miller, J. Am. Chem. Soc., **52**, p. 42; 1930.

mate, either in color or in osmium content, the latter being brown rather than yellow, and containing about 15.8 per cent of osmium as compared with about 19.1 per cent for the compound prepared from the chloroosmate. These values for the osmium content are not to be regarded as accurate. They are probably slightly high because they were determined from the weight of osmium actually taken and the weight of the precipitate formed, without correcting for the small amount of osmium left in the filtrates. However, they are amply accurate to indicate a real difference in composition between the two precipitates. Also, in the case of the compound prepared from the chloroosmate, the value differs too much from the value given by Ogburn and Miller to warrant the opinion that the composition of the compound is definite enough, except possibly under very closely regulated conditions, to permit determining osmium by the use of an arbitrary factor.

The two compounds formed were qualitatively examined for the presence of chlorine and bromine with the expectation of accounting for the differences in color and osmium content. Quite contrary to the findings of the authors that their compound contained no chlorine, the two compounds were found to yield considerable amounts of halogen. In view of the inconstancy of composition of the precipitates, and because of the failure to get quantitative precipitation, it appeared that the method proposed by Ogburn and Miller could not be regarded as reliable, at least in its present form.[20]

II. OBJECT OF THE INVESTIGATION

The object of the experiments reported in this paper was the development of an accurate method for the determination of osmium which would be as simple and as rapid as possible. As seen from the previous discussion no satisfactory method had so far been developed.

The determination of osmium in a material, such as crude platinum, osmiridium, etc., ordinarily involves solution of the original material; separation of osmium from accompanying elements, usually by distillation as tetroxide; absorption of the tetroxide in some reagent solution with subsequent recovery of the osmium and its conversion to a weighable form. It has been generally assumed that the separation of osmium from other elements by distillation of osmium tetroxide is complete, but the literature does not disclose any thoroughgoing quantitative study of this subject. The experiments reported here were directed principally toward a method determination, but incidental work was done to determine the completeness of the separation of osmium by the usual method of distillation. The experiments were not extended to methods of effecting solution of raw platiniferous materials.

[20] In view of the behavior of strychnine in forming salts by direct addition of acids, it is interesting to speculate whether, in its reaction with osmium (and the known reactions with the other platinum metals), strychnine is not acting simply like the ammonium radicle and forming strychnine chloroosmate $(C_{21}H_{22}O_2N_2)_2{-}H_2OsCl_6$, and strychnine bromoosmate, $(C_{21}H_{22}O_2N_2)_2{-}H_2OsBr_6$. The properties of the compounds tend to suggest this structure and the calculated osmium content of strychnine chloroosmate, 17.76 per cent, corresponds much more closely with Ogburn and Miller's average value 17.58 per cent, than does the osmium content of the compound postulated by them. If such compounds were being precipitated from solutions of ammonium or alkali chloroosmate or bromoosmate it is not impossible that mixed crystals of the strychnine and these ammonium or alkali compounds would be formed. The formation of mixed crystals with the less soluble ammonium or potassium salts would be more likely than with the very soluble sodium salts. The presence of such mixed crystals in the preparation referred to in this paper would account for its having a greater osmium content than that calculated for strychnine chloroosmate and that of the preparation of Ogburn and Miller.

III. PREPARATION OF OSMIUM COMPOUNDS FOR USE IN THE EXPERIMENTS

The osmium used was purified by the method described in an earlier paper [21] from this laboratory. The osmium was distilled from a solution containing nitric acid, the tetroxide absorbed in a solution of sodium hydroxide and the distillation and absorption repeated. The alkaline osmate solution from the second distillation was neutralized with hydrochloric acid and the osmium recovered as hydrated osmium dioxide. This product was washed with water by decantation and sucked as dry as possible on a filter. The dioxide was reduced to metallic osmium by strong ignition in hydrogen.[22] The reduced metal, which was free from the other platinum metals, was carefully ignited to osmium tetroxide in a current of oxygen. The tetroxide was recovered by condensation and converted, in one instance, into chloroosmic acid, (H_2OsCl_6) and in the other, into bromoosmic acid (H_2OsBr_6).

The conversion of the tetroxide into chloroosmic acid was accomplished by heating the tetroxide with four times the theoretical quantity of 6 normal hydrochloric acid to which about 5 ml of alcohol had been added. The reaction flask was connected to a reflux condenser by a ground-glass joint. The end of the reflux condenser was fitted to a trap containing a solution of sodium hydroxide and alcohol to catch the small amount of osmium tetroxide which passed the condenser. The reaction mixture was heated gently at first and the temperature very gradually increased during three hours to incipient boiling. The osmium tetroxide was gradually reduced to quadrivalent osmium chloride, completion of the reaction being shown by the absence of droplets of osmium tetroxide condensing on the walls of the flask, the change of color of the solution to a clear transparent red, and the absence of the characteristic odor of osmium tetroxide. The solution of chloroosmic acid was evaporated to a sirup on the steam bath and then twice evaporated with hydrochloric acid (specific gravity 1.18). The sirupy residue was dissolved in dilute hydrochloric acid (1 volume of acid of specific gravity 1.18 diluted with 9 volumes of water) and filtered through paper. Ammonium chloroosmate was precipitated by slowly adding a saturated solution of ammonium chloride to this solution. The brick-red precipitate was caught on a hardened filter and washed first with a solution of ammonium chloride and finally with alcohol. The precipitate was sucked as dry as possible, dried over phosphorus pentoxide in a desiccator for some time, then intimately mixed by grinding in an agate mortar, and stored over phosphorus pentoxide in a desiccator until used.

The conversion of osmium tetroxide into bromoosmic acid and finally into ammonium bromoosmate was accomplished in the same manner as described for the chloro compound, the difference being that hydrobromic acid was used in place of hydrochloric acid. The reduction with hydrobromic acid takes place more readily than with

[21] E. Wichers, R. Gilchrist, and W. H. Swanger, Trans. Am. Inst. Mining Met. Eng., **76**, p. 602; 1928.

[22] Later experience has shown that this procedure is probably not desirable because of danger of deflagration. In the work here reported the presence of sodium chloride, resulting from incomplete removal by washing, no doubt prevented deflagration. It would be better to impregnate the precipitate with ammonium chloride prior to drying and ignition, or alternatively to dissolve the precipitate in hydrochloric acid and precipitate the osmium as ammonium chloroosmate.

hydrochloric acid. Ammonium bromoosmate is deep brown, almost black in color and forms a deep brown solution in water.

It is perhaps needless to mention that no attempt was made to prepare compounds of definite composition, but merely to prepare compounds which could be ignited directly to pure osmium. The osmium content of the samples used was never calculated from the theoretical formula, but was always determined whenever a series of samples was weighed. For this purpose a few samples were taken at random and ignited to metal in hydrogen. The sample was placed in a porcelain crucible which was then covered with a perforated quartz lid. A gentle flame was directed against the top of the lid and a stream of hydrogen, burning from the tip of a quartz delivery tube, was introduced through the hole in the lid. After about 10 minutes a second flame was placed beneath the crucible, and the osmium salt was slowly and very cautiously decomposed. When the resulting metallic sponge began to contract, the temperature of the second flame was gradually increased to that of the full heat of the burner. After 20 minutes both flames were removed and when the crucible had cooled somewhat, the hydrogen flame was extinguished by momentarily breaking the current of hydrogen. The hydrogen was finally displaced by carbon dioxide and the crucible allowed to cool to room temperature. After weighing, the metallic sponge was again heated in hydrogen for 20 minutes and cooled as just described. In so doing no significant changes of weight were observed. The average value found was used to calculate the osmium present in the remaining portions used for experiment.

The values found for the osmium content of the preparations of ammonium chloroosmate and of ammonium bromoosmate used in the investigation are given in Table 1.

TABLE 1.—*Determination of the osmium content of the preparations of ammonium bromoosmate and of ammonium chloroosmate used*

No.	$(NH_4)_2OsBr_6$	$(NH_4)_2OsCl_6$	Osmium	Osmium	Tables
	g	*g*	*g*	*Per cent*	
1	0.5134		0.1440	28.05	2, 3.
2	.4362		.1224	28.06	
3	.3892		.1092	28.06	
4	.5942		.1668	28.07	
5	.4673		.1311	28.05	
6	.3567		.1001	28.06	
				28.06	
7	.3946		.1063	26.94	4, 5.
8	.4915		.1322	26.90	
9	.4161		.1119	26.89	
				26.91	
10	.4818		.1297	26.92	3, 5, 7.
11	.5729		.1544	26.95	
12	.6789		.1830	26.95	
				26.94	
13		0.4482	.1760	39.27	2.
14		.7449	.2927	39.29	
				39.28	
15		.2550	.1111	43.42	3.
16		.2561	.1112	43.42	
17		.2346	.1018	43.39	
				43.41	

IV. PRECIPITATION OF HYDRATED OSMIUM DIOXIDE BY HYDROLYSIS

Preliminary experiments were made in which hydrated osmium dioxide was precipitated, according to the directions of Ruff and Bornemann, from solutions of sodium hydroxide containing some alcohol to which were added known quantities of chloroosmic acid (H_2OsCl_6). The precipitate, in each instance, was caught on an asbestos filter in a porcelain crucible and reduced in hydrogen, the crucible being covered with a perforated quartz lid and shielded from the burner flame by a second crucible. Deflagration of the precipitate nearly always occurred within one or two minutes after the introduction of the burning hydrogen and before heat was applied to the under side of the protecting crucible. In some instances no deflagration occurred. Here it was found that the weight obtained after strong ignition in hydrogen was excessively high. No consistent results could be obtained, and on ignition the metallic residues were found to be contaminated with silica, those which did not deflagrate showing the greatest contamination.

After these preliminary experiments the work on osmium was interrupted by similar work on a method for the determination of ruthenium.[23] In the experiments with ruthenium it was found that quantitative precipitation by hydrolysis could be easily and quickly accomplished from the acid side and that the precipitate was not contaminated by silica or by alkali. Furthermore, it was found that the presence of ammonium salts eliminated the danger of deflagration when the dried precipitate was ignited.

By following the procedure developed for ruthenium, the difficulties previously encountered with osmium vanished and excellent recoveries were obtained. In one experiment, where a Munroe crucible was used instead of a Gooch crucible, 0.01305 g of osmium as H_2OsCl_6 was taken, and 0.0130 g was recovered. In a second similarly conducted experiment in which ten times the quantity of osmium was taken, 0.1305 g of osmium was recovered. The technic of handling the precipitated osmium dioxide differed somewhat from that with the ruthenium oxide and will be discussed more fully in a later section of this paper.

V. EFFECT OF EXPOSURE OF OSMIUM SPONGE TO THE AIR

Since the osmium obtained, both by direct ignition of the ammonium compounds and by ignition of the recovered dioxide, is weighed as metallic sponge it is important to know just what effect exposure to the air has upon the sponge. It had been observed in this laboratory that osmium sponge, produced by igniting ammonium chloroosmate or ammonium bromoosmate in hydrogen in a combustion tube, glowed and emitted pungent vapors of osmium tetroxide when the tube was opened, even at room temperature. If, however, the hydrogen had been displaced by dry purified nitrogen while the osmium sponge was hot and the metal had been allowed to cool in nitrogen no odor of osmium tetroxide was observed and the sponge suffered no change in weight on standing in the air for some time.

[23] See footnote 18, p. 426.

In the procedure used in the experiments reported here the osmium was not ignited in a combustion tube but in a crucible, either of porcelain or of platinum, and carbon dioxide was used to displace the atmosphere of hydrogen. In order to ascertain the reproducibility of weight when such a procedure was followed, portions of osmium sponge, resulting from the reduction of ammonium bromoosmate, were repeatedly ignited in hydrogen, cooled in carbon dioxide, and weighed. It was found that no significant changes of weight occurred during such operations and in addition that no changes of weight were observed, even when the sponge had remained in a desiccator over a period of two weeks.

VI. QUALITATIVE EXPERIMENTS TO DETERMINE THE COMPLETENESS OF PRECIPITATION OF HYDRATED OSMIUM DIOXIDE

It was observed, as it was with ruthenium, that as the boiling acidified solution of osmium was gradually neutralized by the addition of sodium bicarbonate, a precipitate suddenly coagulated and settled. With ruthenium, this coagulation and separation represented complete precipitation. Qualitative experiments were made to determine whether the same was true with osmium. Portions of ammonium bromoosmate were dissolved in 150 ml portions of water. A 10 per cent solution of sodium bicarbonate was slowly added to the boiling solutions until coagulation occurred. One solution was then boiled for 15 minutes and the other for 6 minutes and filtered through S. and S. No. 589 blue ribbon paper. The filtrates were colorless and clear, and had acidities which were between the pH values 1.5 and 4.0. A sample of ammonium chloroosmate was also treated as described and the solution boiled for six minutes. In this instance the acidity of the water clear filtrate was estimated, by means of indicator solutions, to be approximately 2.8 to 3.0. The filtrates were tested for the presence of osmium by means of thiourea as described in a subsequent paragraph. No osmium was detected in any of the filtrates.

An experiment was also made to determine whether a loss of osmium as osmium tetroxide occurred during hydrolysis. In this instance the neutralization with sodium bicarbonate was done in a distilling apparatus composed wholly of glass and the solution was finally boiled for one-half hour while a slow current of air was passed. The vapors which distilled were absorbed in a solution of 6 normal hydrochloric acid saturated with sulphur dioxide to which thiourea was added. This solution developed no pink color when heated. As 0.1 mg of osmium would have been readily detected, it was evident that no loss occurred.

VII. DETECTION OF MINUTE QUANTITIES OF OSMIUM BY REACTION WITH THIOUREA

It very soon became necessary to be able to detect small quantities of osmium, particularly in the filtrates from hydrolysis and in the residual nitric acid solutions after osmium had been distilled as tetroxide.

The most delicate known reaction for the detection of osmium is that discovered by Chugaev [24] during his researches on osmium compounds. Chugaev found that when a solution containing osmium tetroxide or potassium chloroosmate, acidified with a few drops of hydrochloric acid, is heated with thiourea for a few minutes a deep red or rose color develops. He also found the limit of sensitivity to be 1 part in 100,000 parts of solution.

The test as described by Chugaev, however, can not be applied directly to a solution containing a considerable quantity of nitric acid, since this acid decomposes the reagent. It was found, however, that if the nitric acid is destroyed by reaction with sulphur dioxide the color with thiourea will develop and be stable. Experiments with known quantities of osmium showed that under these conditions the limit of sensitivity is 1 part in 5,000,000 parts of solution, and

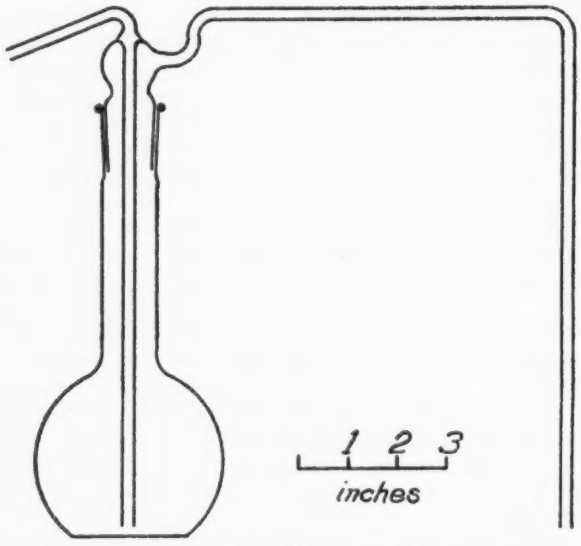

FIGURE 1.—*Distilling flask for osmium tetroxide*

that for concentrations greater than 1 part in 2,500,000 the pink color develops in less than 15 minutes. The sulphur dioxide may be conveniently added in the form of solution in water, and it is well to have it present in excess. Only a few small crystals of thiourea are required, and it is necessary only to heat the solution on the steam bath.

The presence of indicators, such as brom cresol purple, brom phenol blue, etc., masks the color produced by thiourea so that when filtrates from hydrolysis were being investigated the osmium had to be removed by distillation with nitric acid from an apparatus composed wholly of glass (shown in fig. 1) and absorbed in a solution of 6 normal hydrochloric acid saturated with sulphur dioxide and containing a little thiourea. The distillation of osmium tetroxide was aided by passing a current of air through the apparatus.

[24] L. Chugaev, Compt. rend., **167**, p. 235; 1918.

VIII. CHOICE OF CRUCIBLES FOR FILTRATION

In gravimetric procedures for determining osmium it is obviously impossible to use filter paper, because oxidation of osmium to the volatile tetroxide will occur when the paper is destroyed by ignition in air.

In the methods discussed in the introductory part of this paper, filtering tubes containing pads of asbestos were used to recover the precipitate of osmium dioxide. It was found that a Gooch crucible with an asbestos pad, prepared in the usual way and ignited to constant weight, can be used. Care must be taken, however, in the preparation of the asbestos used as a filter. In a series of five experiments, in which the hydrated osmium dioxide was hydrolyzed from solutions of ammonium chloroosmate at pH values ranging from 4.0 to 6.3, it was observed that a small quantity of precipitate passed through the asbestos filters. The errors found were from -0.0001 to -0.0010 g of osmium on 0.20 to 0.24 g of osmium taken, and these amounts were readily detected in the filtrates. In a second, more carefully conducted, series of five experiments, in which the hydrated dioxide was precipitated from solutions of ammonium bromoosmate at pH values ranging from 4.0 to 6.0, the errors observed in four of the experiments varied from $+0.0001$ to -0.0001 g of osmium, while in the fifth the error was -0.0003 g. When these filtrates were filtered through S. & S. No. 589 blue ribbon papers, no blackening of the papers was observed except in the case of the one showing the error -0.0003 g.

The chief disadvantage in the use of a Gooch crucible with an asbestos pad is the difficulty encountered during the ignition of the dioxide to metal. Even when the Gooch crucible is protected from the burner flame by setting it in a circle of asbestos board in a larger porcelain crucible, one is not always able to extinguish the hydrogen flame readily. Experiments, made in an attempt to eliminate the use of carbon dioxide by cooling the sponge in hydrogen in order to simplify technic, showed that frequently the apparently cold metal would become warm and emit odors of tetroxide. The cause for such behavior was most probably the diffusion of air to the metal sponge through the holes in the bottom of the crucible.

For accurate work the Munroe crucible, which is of platinum and has a filter consisting of platinum sponge, was found to be preferable to the Gooch crucible with a filter of asbestos. A crucible of this kind was used in most of the experiments reported here. No precipitate was ever observed to have escaped this filter. A platinum cap, which fitted the bottom of the Munroe crucible, eliminated the necessity for a second protecting crucible. The ignition of the dioxide and the cooling of the resulting metal were greatly simplified when this type of crucible was used.

IX. RANGE OF pH VALUES OVER WHICH HYDRATED OSMIUM DIOXIDE IS COMPLETELY PRECIPITATED BY HYDROLYSIS

In a study on ruthenium it was found that for complete precipitation by hydrolysis the acidity of the solution could not deviate far from the value pH 6.0.

The qualitative experiments with osmium, described in a preceding section of this paper, indicated that a greater latitude of acidity was permissible for osmium and that complete precipitation occurred between pH 1.5 and 6.3. On either side of these limiting values the hydrated osmium dioxide tended to become colloidal. In order to confirm these qualitative observations, seven quantitative experiments were made in which known pH values were established by the use of indicator solutions. A solution of sodium bicarbonate was added to the boiling solutions containing the osmium until the indicator just changed color. The solutions were then boiled for about six minutes and filtered through a Munroe crucible. The precipitates were thoroughly washed with a hot 1 per cent solution of ammonium chloride, impregnated with saturated ammonium chloride, dried carefully, ignited in hydrogen, and the metal produced cooled to room temperature in carbon dioxide.

The complete transfer of the precipitate from the beaker to the crucible was effected by using a well-wetted policeman, since paper could not be used. Experience showed that this practice introduced no appreciable error into the determination. The filtrates from hydrolysis were found to be free from osmium when tested as previously described. The optimum pH for quick settling appeared to be about 4. This is the acidity at which brom phenol blue indicator changes from yellow to blue, and is the one which was always established in subsequent experiments.

The quantitative results are given in Table 2. The error in No. 21 was caused by a slight deflagration during ignition of the precipitate in hydrogen.

TABLE 2.—*Range of pH values over which hydrated osmium dioxide is completely precipitated by hydrolysis*

No.	$(NH_4)_2OsBr_6$ 28.06 per cent Os	$(NH_4)_2OsCl_6$ 39.28 per cent Os	Osmium present	Osmium recovered	Error	Indicator used	pH
	g	*g*	*g*	*g*	*g*		
18	0.4449		0.1248	0.1248	0.0000	Thymol blue	1.5
19	.4663		.1308	.1308	.0000	Brom phenol blue	4.0
20	.4599		.1290	.1289	−.0001	Brom cresol green	4.7
21	.4444		.1247	.1239	−.0008	Chlor phenol red	6.0
22	.4023		.1129	.1129	.0000	Brom cresol purple	6.3
23		0.2823	.1109	.1107	−.0002	Thymol blue	1.5
24		.2679	.1053	.1052	−.0001	Brom phenol blue	4.0

X. SEPARATION OF OSMIUM BY DISTILLATION AND RECOVERY BY HYDROLYSIS

The method developed in the foregoing experiments for the recovery of osmium is applicable to solutions which contain no other heavy metals. When other metals are present it becomes necessary first to make a separation of the osmium from these elements. The usual procedure described in the literature is to add nitric acid to such a solution, distil the osmium as tetroxide and absorb it in a solution of sodium hydroxide containing some alcohol.

Two experiments were made to test this method of separation by distillation with subsequent recovery of the osmium from the solution of sodium hydroxide. The apparatus used consisted of a

1-liter flask and four Erlenmeyer receiving flasks, each of 300 ml capacity. The entire apparatus was of glass and the various parts were connected by carefully ground joints. The distilling flask was provided with an inlet through which a slow current of air was passed during distillation and a thistle tube, having a stopcock, for the introduction of nitric acid. This stopcock was lubricated with vaseline. All other ground joints were sealed with a film of water. The evolved tetroxide was absorbed in a 10 per cent solution of sodium hydroxide to which one-fifth of its volume of alcohol was added. The absorption of the tetroxide appeared to be nearly complete in the solution in the first flask, and no osmium escaped the train of receiving solutions. The united solutions were digested on the steam bath for some hours to insure the complete reduction of the tetroxide. The osmium was recovered by hydrolysis in the manner previously described, after the alkaline solutions had been made acid with hydrochloric acid. In one experiment only about one-third of the osmium taken as ammonium bromoosmate was recovered. In the other experiment the recovered quantity was in excess of that taken by over 12 per cent. This abnormal result was found to have been caused by the presence of silica, dissolved from the glass by the hot alkaline solution. The osmium actually present in the contaminated precipitate, determined by difference on ignition in oxygen, was only 80 per cent of that originally taken. The incomplete recoveries were attributed to the presence of nitrates formed during the distillation of the osmium tetroxide. When the alkaline solutions were made acid with hydrochloric acid an indefinite amount of osmium must have escaped, since the filtrates from the hydrolytic precipitations showed no appreciable quantity of osmium.

While the removal of the osmium from the distilling flask was apparently complete and the absorption of the osmium tetroxide in the alkaline solutions quantitative, it did not appear hopeful to adapt the method of hydrolysis from acid solution to the final recovery of the osmium. It became necessary, therefore, to consider other absorbent solutions.

The use of hydrobromic acid in the preparation of bromoosmic acid suggested the possibility of using this reagent as an absorbent. Experiments, in which a 20 per cent solution of hydrobromic acid to which one-fifth of its volume of alcohol was added, proved definitely that absorption of osmium tetroxide in this reagent was not quantitative, even when the solutions were kept hot. The recoveries were found to be low by an amount varying from 5 to 24 per cent of the osmium taken, and appreciable quantities of osmium tetroxide were readily detected escaping the train of receiving solutions.

It was clearly apparent from the experiments with sodium hydroxide that the nitric acid which distilled with the tetroxide interfered in the subsequent recovery of the osmium. In order to eliminate this source of error it was necessary to destroy any nitric acid which entered the receiving solutions. In addition, it was advantageous to produce a solution to which the newly developed hydrolytic procedure could also be applied. A solution of both of these problems appeared to be offered by using 6 normal hydrochloric acid which had been saturated with sulphur dioxide.

Experiments were then made using this reagent as the absorbent. In the first experiment 0.1519 g of osmium as ammonium bromoosmate was taken. One hundred milliliters of water and 50 ml of nitric acid (specific gravity 1.42) were placed in the distilling flask. Each of three receiving flasks contained 75 ml of the absorbent reagent. The solution in the distilling flask was colorless after one hour. The complete absence of osmium in the residual nitric acid solution was proved, as previously outlined, by a negative test with thiourea when the nitric acid was destroyed by sulphur dioxide. No osmium was detected having escaped the train of receiving solutions. The contents of the three receiving flasks were united and evaporated on the steam bath to a volume of about 2 to 3 ml.[25] The quantity of osmium recovered by hydrolysis was 0.1497 g, or 98.55 per cent of the quantity taken.

In the second experiment 0.1735 g of osmium as ammonium bromoosmate was taken. Each of two receiving flasks contained 200 ml of the absorbent solution. The third flask, in this instance, was used for the detection of osmium by thiourea. Distillation was continued for 1 hour, 10 minutes. No osmium escaped the second receiving flask, but a small quantity, estimated by the intensity of color developed with thiourea to be about 0.00024 g, was found in the nitric-acid solution after distillation was thought to be complete. There was recovered from the solution in the first receiving flask 0.1677 g of osmium, and from that in the second receiving flask 0.0030 g of osmium. The remaining 0.0026 g of osmium could not be accounted for.

In the third experiment 0.1106 g of osmium as ammonium bromoosmate and, in addition 0.1 g of iridium as ammonium chloroiridate, were taken. In this and in subsequent experiments the quantity of nitric acid used was reduced to 20 ml. At the end of one hour the solutions in the three receiving flasks were replaced by fresh solutions of 6 normal hydrochloric acid saturated with sulphur dioxide. Distillation was then continued for three-fourths hour. No color developed in the second set of solutions and, on evaporation of these solutions to a volume of about 5 ml, thiourea detected no osmium present. From the first set of absorbing solutions 0.1094 g of osmium was recovered, less than the quantity taken by 0.0012 g.

In a fourth experiment 0.0956 g of osmium as ammonium chloroosmate, together with a total quantity, 0.3 g, of Pt, Ir, Rh, and Pd as chlorides, was taken. The distillation was continued for seven hours, using four renewals of absorbent solution. The unexpectedly slow distillation of osmium from the chloroosmate will be discussed in a later section. The quantity of osmium recovered from the united receiving solutions was 0.0929 g, differing from the quantity taken by 0.0027 g.

In these experiments an error, amounting usually to less than about 2.5 mg of osmium, irrespective of the quantities of osmium taken, continued to occur in the recovery of osmium by distillation with nitric acid.

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[25] It may occur to the reader that the osmium could be recovered from the absorbent solution more simply by igniting the evaporated residue under hydrogen without resorting to a hydrolytic precipitation. In such a procedure it would be necessary to neutralize the sulphuric acid present. This could be done by adding a slight excess of ammonium chloride during evaporation. The subsequent evaporation and drying of the salt mixture in a crucible, simple as it at first appears, is very troublesome, however, because of the marked tendency of the ammonium salts to creep. Furthermore, this creeping would enhance the danger of loss of osmium. Also such a method of treatment would not eliminate impurities in the form of soluble salts introduced through the reagents used and would be wholly unsuitable if applied as a general method to solutions containing appreciable quantities of alkali salts. The recovery of osmium by hydrolysis, on the other hand, obviates these difficulties without requiring additional time.

XI. EXPERIMENTS TO LOCATE THE SOURCE OF ERROR IN THE DETERMINATION OF OSMIUM BY DISTILLATION FROM SOLUTION WITH NITRIC ACID

While the results obtained when 6 normal hydrochloric acid saturated with sulphur dioxide was used as an absorbent solution were gratifying, they were not quantitatively satisfactory. There repeatedly appeared a small but significant error, the cause of which was not immediately apparent. Precaution had been taken to flush frequently the tube used for the introduction of nitric acid into the distilling flask so that it was not likely that the discrepancies in recovery were occasioned by loss of tetroxide diffusing into this tube. A new distilling and receiving apparatus, meanwhile, was so constructed that the possibility of loss of osmium tetroxide by leakage was thought to have been eliminated. Experiments were repeated with this new apparatus and again errors of the same magnitude as those previously observed were obtained.

Attention was then turned to another possible cause for the error observed; namely, loss of osmium as tetroxide when the absorbent solutions were evaporated on the steam bath. If this were the cause, losses of osmium should occur with solutions made to approximate in composition those actually obtained on distillation.

Two series of such solutions were prepared. In the one, portions of ammonium chloroosmate and of ammonium bromoosmate were each dissolved in 250 ml of 6 normal hydrochloric acid and the solutions evaporated on the steam bath until dry residues of salt were obtained. These residues were dissolved in 150 ml portions of water, the solutions heated to boiling, and the osmium precipitated by hydrolysis at pH 4.0. The precipitates were filtered on a Munroe crucible, washed with a hot 1 per cent solution of ammonium chloride, impregnated with saturated ammonium chloride, ignited in hydrogen, cooled in carbon dioxide and weighed. The results, given in Table 3, showed that no significant losses of osmium occurred under these conditions.

TABLE 3.—*Recovery of osmium from solutions of ammonium chloroosmate and of ammonium bromoosmate in 6 normal HCl evaporated to dryness*

No.	$(NH_4)_2OsBr_6$	$(NH_4)_2OsCl_6$	Osmium present	Osmium present	Osmium recovered	Error
	g	*g*	*Per cent*	*g*	*g*	*g*
25	----------	0.2584	43.41	0.1121	0.1124	+0.0003
26	0.3537	----------	28.06	.0993	.0993	.0000
27	.5041	----------	26.94	.1358	.1357	−.0001
28	.6407	----------	26.94	.1726	.1725	−.0001

In the second series, solutions were made so as to duplicate those obtained when the distilled osmium tetroxide was absorbed in 6 normal hydrochloric acid saturated with sulphur dioxide. For this purpose, portions of ammonium bromoosmate were added to solutions composed of 250 ml of 6 normal hydrochloric acid, 2 ml of sulphuric acid (specific gravity 1.84) and 100 ml of water which had been saturated with sulphur dioxide. These solutions were allowed to remain on the steam bath for several hours after no further evaporation occurred. The solutions, which were sirupy because of the sulphuric

acid present, were diluted to 150 ml with water and the osmium recovered as above described. The sirupy solutions, previous to dilution, were frequently smelled, but no odor of tetroxide was ever observed. The recoveries of osmium obtained, shown in Table 4, were practically quantitative in 2 of the 6 experiments, but in the other 4 were low by amounts which approximated those previously observed.

TABLE 4.—*Recovery of osmium from solutions of ammonium bromoosmate in 6 normal HCl to which H_2SO_4 and SO_2 were added*

No.	$(NH_4)_2OsBr_6$ 26.91 per cent Os	Osmium present	Osmium recovered	Error
	g	*g*	*g*	*g*
29	0.4624	0.1244	0.1245	+0.0001
30	.4974	.1339	.1325	−.0014
31	.5032	.1354	.1334	−.0020
32	.4691	.1262	.1248	−.0014
33	.4574	.1231	.1213	−.0018
34	.4640	.1249	.1246	−.0003

It seemed strange, if losses of osmium occurred on evaporation, especially when the solutions became sirupy, that they showed no particular increase when the concentrated solutions were allowed to remain on the steam bath. If the sulphuric acid present were really responsible for the discrepancy between the quantity of osmium taken and that recovered, it was thought that neutralization of the acid by the formation of sulphate might decrease the magnitude of the error. Consequently, portions of ammonium bromoosmate were dissolved in solutions composed of 250 ml of 6 normal hydrochloric acid, 2 ml of sulphuric acid (specific gravity 1.84), and 100 ml of water which had been saturated with sulphur dioxide. In order to provide for the neutralization of the sulphuric acid when the solutions became concentrated, 5 g of sodium chloride was added to each of four solutions and 5 g of ammonium chloride to each of two solutions. These salts were added in the form of filtered solutions. The six solutions were allowed to evaporate to dryness and the beakers were then left several hours on the steam bath. The dried residues were dissolved in water as before and the osmium recovered by hydrolysis in the manner already described. The recoveries, as shown in Table 5, were nearly complete in three of the experiments, but in the other three were low by amounts approximating those previously observed.

TABLE 5.—*Recovery of osmium from solutions of ammonium bromoosmate in 6 normal HCl to which H_2SO_4, SO_2, NaCl and NH_4Cl were added*

No.	$(NH_4)_2OsBr_6$	Osmium present	Osmium present	Osmium recovered	Error	
	g	*Per cent*	*g*	*g*	*g*	
35	0.3716	26.91	0.1000	0.0974	−0.0025	NaCl.
36	.4697	26.91	.1264	.1264	.0000	
37	.3847	26.94	.1036	.1034	−.0002	
38	.4288	26.94	.1155	.1152	−.0003	
39	.5044	26.94	.1359	.1329	−.0030	NH_4Cl.
40	.5266	26.94	.1419	.1408	−.0011	

The sole remaining source of error was the incomplete precipitation of the osmium on hydrolysis. It had been previously established by experiment that no significant amount of osmium remained in the filtrates, but the conditions were different in that no sulphur dioxide had ever been present. The filtrates obtained in the experiments reported in Tables 3, 4, and 5 were now carefully searched for the presence of osmium. These filtrates were water clear and showed no evidence of osmium dioxide depositing on standing. Each filtrate in turn was completely transferred to the distilling apparatus. Twenty milliliters of nitric acid (specific gravity 1.42) was added and the solution heated to boiling for one-half hour while a slow current of air was passed. The distillate, in each instance, was led into 50 ml of 6 normal hydrochloric acid saturated with sulphur dioxide to which thiourea was added. When the solutions were heated on the steam bath intensities of color developed which corresponded to the magnitude of the observed errors. The results obtained are assembled in Table 6.

TABLE 6.—*Detection of osmium in the filtrates from hydrolysis of absorbent solutions containing sulphur dioxide*

No.	Error	Color produced by reaction with thiourea
	g	
25	+0.0003	Colorless.
26	.0000	Do.
27	−.0001	Faint pink.
28	−.0001	Colorless.
29	+.0001	Faint pink.
30	−.0014	Red.
31	−.0020	Strong red.
32	−.0014	Red.
33	−.0018	Do.
34	−.0003	Faint pink.
35	−.0026	Strong red.
36	.0000	Colorless.
37	−.0002	Faint pink.
38	−.0003	Do.
39	−.0030	Deep red.
40	−.0011	Red.

XII. COMPLETE RECOVERY OF OSMIUM FROM SOLUTIONS OF HYDROCHLORIC ACID WHICH HAVE CONTAINED SULPHUR DIOXIDE

The source of the slight error in the determination of osmium, when the solution consisting of 6 normal hydrochloric acid saturated with sulphur dioxide was used for the absorption of the evolved tetroxide, was thus traced to the incomplete precipitation of the osmium on subsequent hydrolysis. The cause of the incomplete precipitation was attributed to the presence of a small quantity of an undecomposed sulphite compound of osmium. It had been demonstrated that if no sulphur dioxide was used, precipitation was quantitative and that no significant amount of osmium remained in the filtrate. Furthermore, in considering various reagent solutions to absorb osmium tetroxide, it was observed that while a solution of sodium sulphite completely absorbed the tetroxide only a very slight precipitate was obtained on subsequent hydrolysis.

In order, then, to effect quantitative precipitation it would be necessary to insure the complete destruction of any sulphite compounds of osmium. Accordingly, three solutions were prepared, containing ammonium bromoosmate, hydrochloric acid, sulphuric acid, sulphur dioxide, and water as previously described, and evaporated as far as possible on the steam bath. Each sirupy residue was digested for about 15 minutes with 10 ml of hydrochloric acid (specific gravity 1.18) and again evaporated. The digestion with 10 ml of hydrochloric acid and evaporation were repeated. The residues from the last evaporation were diluted with 150 ml of water. During precipitation the solutions were purposely maintained at nearly boiling temperature for approximately four hours while the bicarbonate was being added. This was done, incidentally, to confirm previous observations that no loss of osmium as osmium tetroxide occurred during hydrolysis. When the brom phenol blue indicator present turned faintly blue, the solutions were boiled six minutes.

The precipitate in experiment No. 41 was filtered immediately. Those in Nos. 42 and 43 were not filtered until 48 hours later. Just previous to filtration these latter two were again boiled for five minutes. The metallic residues from Nos. 42 and 43 were well washed with a hot 1 per cent solution of ammonium chloride and ignited again in hydrogen. The weights remained constant, showing that the washing of the original precipitate had been complete. The three filtrates were tested for osmium as previously described. A faint pink color developed in each instance which corresponded to a quantity of osmium far less than 0.0001 g.

The results, given in Table 7, which were later confirmed by experiments described in Section XIV, showed that digestion of the sirupy residue with hydrochloric acid eliminated the cause of error. Incidentally, the results given in Table 7 showed that no osmium was lost on prolonged boiling of the solutions during the neutralization of excess acid by sodium bicarbonate.

TABLE 7.—*Complete recovery of osmium from solutions of HCl which have contained* SO_2

No.	$(NH_4)_2OsBr_6$ 26.94 per cent Os	Osmium present	Osmium recovered	Error
	g	g	g	g
41	0.6712	0.1808	0.1806	−0.0002
42	.5136	.1384	.1385	+.0001
43	.5025	.1354	.1354	.0000

XIII. PRECIPITATION OF OSMIUM IN THE PRESENCE OF SODIUM SALTS

The hydrolytic precipitation of osmium as the hydrated dioxide necessarily always occurred in the presence of varying amounts of sodium chloride or of sodium sulphate, produced by neutralization with sodium bicarbonate of the corresponding acid present in the solutions. These precipitates were always washed thoroughly with a hot 1 per cent solution of ammonium chloride. In nearly every instance the metallic residues obtained after ignition in hydrogen were also washed with this reagent solution and reignited. No

significant differences were ever found in the weights obtained. It thus appeared that a single thorough washing removed all sodium salts. Furthermore, the washing never caused the precipitate to become colloidal.

XIV. SEPARATION OF OSMIUM FROM THE OTHER PLATINUM METALS BY DISTILLATION FROM NITRIC-ACID SOLUTION

With a reliable method at hand for the recovery of osmium from a suitable absorbing solution, the investigation was now extended to the matter of the quantitative separation of osmium from the other platinum metals by distillation as osmium tetroxide. Methods for the determination of osmium, involving the separation of osmium from accompanying metals by distillation as tetroxide from nitric-acid solution, are frequently mentioned in the literature and it has been usually assumed that the separation is complete. However, no specific data resulting from critical experiments could be found to verify this assumption.

To make certain, first of all, that no significant quantities of the platinum metals reached the receiving flasks, either by distillation or by entrainment, a solution containing 0.100 g of platinum, 0.106 g of iridium, 0.082 g of rhodium, and 0.020 g of palladium, as chlorides, was placed in the distilling flask with 150 ml of water and 20 ml of nitric acid (specific gravity 1.42) and boiled for one hour while a slow current of air was passed. The absorbing solution, consisting of 6 normal hydrochloric acid, was evaporated nearly to dryness and diluted with 5 ml of water. No evidence of precipitation was obtained when this colorless solution was treated with hydrogen sulphide. A second solution, containing approximately 0.1 g of ruthenium as chloride, was treated similarly, boiling being continued for two hours, and the distilled vapors caught in 6 normal hydrochloric acid containing some alcohol. The receiving solution was evaporated twice with concentrated hydrochloric acid and finally diluted with 10 ml of water. The thiosulphate test, which is sensitive to extremely small quantities of ruthenium, was applied but no color developed.

Two experiments were made in which osmium was separated from the other five platinum metals by distillation from nitric-acid solution. The quantities of these other metals taken for each experiment were 0.100 g Pt, 0.200 g Ir, 0.016 g Rh, 0.020 g Pd, and 0.075 g Ru. The osmium was distilled from a solution whose volume was 170 ml, of which 20 ml was nitric acid (specific gravity 1.42). The evolved tetroxide was absorbed in 6 normal hydrochloric acid saturated with sulphur dioxide and the metal recovered as previously described. The residual solutions from the distillation yielded no trace of osmium upon further distillation and were in all probability completely free from osmium. In the first experiment, of 0.1608 g of osmium, taken as ammonium bromoosmate, 0.1606 g was recovered. The filtrate obtained upon the precipitation of the hydrated dioxide showed the presence of a minute quantity of osmium, but very much less than 0.0001 g. In the second of these two experiments the quantity of osmium recovered was only 0.2047 g while that taken was 0.2076 g. From 0.002 to 0.0025 g of osmium was found in the filtrate from hydrolysis. The appearance of this quantity of osmium in the filtrate

indicated that the complete destruction of sulphite compounds had probably not been effected previous to hydrolysis. Consequently, two more determinations were made and particular attention was paid to the evaporation of the absorbent solutions. Four additions of concentrated hydrochloric acid were made, instead of two, and each time digestion was prolonged for 15 minutes while the beakers were covered before allowing the solutions to evaporate. The quantities of osmium taken as ammonium bromoosmate were 0.1390 and 0.1548 g and those recovered were 0.1388 and 0.1546 g. No osmium appeared to remain in the residual platinum metal solutions. One of the filtrates yielded a very faint pink color when tested for osmium by distilling into a thiourea solution while the other gave no indication of the presence of osmium.

These results show that the separation of osmium from the other platinum metals by distillation as tetroxide from nitric-acid solution is complete, and that if care is taken to insure total decomposition of sulphite compounds formed during absorption of the tetroxide the recoveries are also quantitative within experimental error.

XV. INCIDENTAL EXPERIMENTS

The elimination of osmium from solutions of ammonium bromoosmate by dilute nitric acid was usually found to be complete within one hour, while the elimination of osmium from solutions of ammonium chloroosmate, under similar conditions, was complete only after seven or eight hours. In an attempt to shorten the time required to effect the separation of osmium from the chloroosmate a number of experiments were made in which the nature or composition of the solution was altered. In addition, observations were also made regarding the behavior of the other platinum metals.

1. DISTILLATION FROM A MIXTURE OF SULPHURIC AND NITRIC ACIDS

A solution containing approximately 0.075 g of osmium as ammonium chloroosmate, 10 ml of sulphuric acid (specific gravity 1.84), 6 ml of 6 normal nitric acid and 25 ml of water was heated in an open beaker. The solution, which emitted heavy vapors of sulphuric acid after 10 minutes, was diluted to 20 ml with water and tested for osmium with thiourea. The complete absence of osmium was demonstrated. The experiment was repeated with a distilling apparatus. At the end of 1 hour the residual solution was colorless and gave no test for osmium with thiourea. The experiment was then repeated in an open beaker, using ammonium bromoosmate instead of ammonium chloroosmate. Again, the osmium was found to be easily eliminated and no osmium remained in the sulphuric acid solution.

When a solution of ruthenium was treated as just described, it was found that as the sulphuric acid approached the fuming stage ruthenium slowly distilled, and that if heating were continued a black deposit appeared in the distilling flask and delivery tube. The successive additions of nitric acid dissolved the black deposit previously formed and caused more and more ruthenium to reach the absorbent solution.

Iridium, taken as ammonium chloroiridate, when treated in the same manner as that described for ruthenium, remained entirely in the distilling flask as a soluble green compound.

2. DISTILLATION FROM SULPHURIC ACID

The experiments which have just been described were repeated with the exception that no nitric acid was used. Here it was found that osmium, originally present as ammonium chloroosmate, was readily and completely eliminated when the solution was heated to the fuming point of sulphuric acid, while that present as ammonium bromoosmate was only partially distilled, the mass remaining in the flask, and likewise in the beaker, as a black deposit. Continued heating for several hours failed to distill more than a small proportion of the osmium taken as bromoosmate.

It was further found that no trace of ruthenium distilled when sulphuric acid alone was used, nor did any iridium. Both of these metals remained in the distilling flask as soluble compounds.

3. DISTILLATION FROM NITRIC ACID

In these experiments the osmium was distilled from concentrated nitric acid. From ammonium bromoosmate the osmium was completely distilled in about 10 minutes while from ammonium chloroosmate the osmium was entirely eliminated only after one and three-fourths hours.

When ruthenium as ammonium nitrosopentachlororuthenate was heated with 100 ml of concentrated nitric acid until 20 ml was volatilized, it was repeatedly found that an appreciable amount distilled. A purplish color was observed in the condensing vapors which passed over at first. Further heating, however, did not cause this phenomenon to continue, nor was ruthenium eliminated at all rapidly from the distilling flask. Noyes and Bray [26] report the observation that no ruthenium distills when a solution containing 4 ml of concentrated nitric acid, 3 ml of residual bromide solution, and 3 ml of water is heated in a distilling flask until 4 ml of liquid has been removed, but that if 2 ml more of liquid is distilled, from 0.0001 to 0.0002 g of ruthenium passes into the distillate. Two experiments were made in which the above conditions were established, but ten times the quantities of materials were used. The vapors were absorbed in 6 normal hydrochloric acid which was constantly saturated with a current of sulphur dioxide. No ruthenium was detected in the first 40 ml of distillate, either by thiourea or by sodium thiosulphate, even when the solutions were concentrated by evaporation to volumes of 5 to 10 ml. A small quantity of ruthenium was found in the next 20 ml of distillate by thiourea in one of the experiments, but the amount was much less than 0.0001 g. No ruthenium could be detected in the second 20 ml portion in the other experiment. A third experiment was made in which no hydrobromic acid was added to the distilling flask. No ruthenium was detected in either portion of distillate by thiourea or by sodium thiosulphate. The distillations were run so that the first 40 ml required about 1 hour 20 minutes and the next 20 ml about 40 minutes.

4. DISTILLATION FROM ALKALINE SOLUTION ACIDIFIED WITH NITRIC ACID

When a metallic material such as osmiridium is fused with a molten mixture of alkali hydroxide and nitrate, the osmium present

[26] Noyes and Bray, Qualitative Analysis for the Rare Elements, The Macmillan Co., p. 41; 1927.

is converted to a soluble osmate. Since this is the form in which the osmium is obtained in the analysis of crude platiniferous material, the following experiment was made to determine the behavior of the osmium on acidification of the solution with nitric acid. It has been generally assumed that the elimination of the osmium as osmium tetroxide under these conditions is quantitative.

Approximately 0.1 g of osmium sponge was added to a molten mixture of 10 g of sodium hydroxide and 1 g of sodium nitrate contained in a gold crucible. The cold alkaline mass was dissolved in 75 ml of water and transferred to the distilling apparatus. A total of 36 ml of nitric acid (specific gravity 1.42) was added and the final volume of the solution became 170 ml. The excess nitric acid produced a colorless solution from which the osmium was easily distilled. The complete absence of osmium in the residual 150 ml of solution was demonstrated, first, by carefully decomposing the nitric acid in a 50 ml portion with sulphur dioxide and testing with thiourea, and, second, by heating a 50 ml portion in a distilling flask and absorbing the vapors in hydrochloric acid, containing thiourea, saturated with sulphur dioxide.

The above experiment was repeated, this time with the addition of 0.093 g of pure iridium sponge. The metallic iridium was added to a molten mixture of 10 g of sodium hydroxide and 2 g of sodium nitrate and appeared to be quite rapidly attacked when the alkaline bath was at a red heat. The melt was maintained at this temperature for 30 minutes, allowed to cool and dissolved, as before, in 75 ml of water. The osmium present was separated in the same manner as described above. At the end of 45 minutes the contents of the distilling flask, consisting of a pale green solution and a black deposit, were transferred to a second distilling flask and heated for 25 minutes. The vapors which distilled were absorbed in a solution of 6 normal hydrochloric acid and thiourea which was saturated with sulphur dioxide. No color developed in this thiourea solution.

To determine whether any osmium was retained by the insoluble iridium compound, the black residue was separated from the supernatant liquor by careful decantation. Twenty millimeters of concentrated sulphuric acid and 2 ml of concentrated nitric acid were added to the flask and the mixture heated for 30 minutes until heavy fumes of sulphuric acid appeared. The distilled vapors, absorbed in a solution containing thiourea, again produced no color. Finally, the insoluble iridium compound was carefully separated from the sulphuric-acid solution by decantation, transferred to a gold crucible, dried by evaporation on the steam bath, and subjected to a second fusion. Upon acidification with nitric acid and distillation, a quantity of osmium, estimated to be not more than 0.0001 g by comparison with solutions of known osmium content, was detected in the thiourea solution.

The foregoing experiments disclosed some rather surprising facts regarding the behavior of chloroosmate and of bromoosmate toward nitric acid and toward sulphuric acid. It was found that chloroosmate was quite stable toward nitric acid, even when the acid was hot and concentrated, but was readily decomposed with complete elimination of osmium by hot concentrated sulphuric acid. On the other hand, bromoosmate was quickly decomposed and the osmium eliminated by nitric acid, both dilute and concentrated, but scarcely

affected by hot concentrated sulphuric acid. A mixture of the two acids, however, quickly eliminated the osmium from either compound. It was further found that while ruthenium did not separate as a volatile compound from hot concentrated sulphuric acid alone, it did so if some nitric acid was present. In addition, it was observed that a small but appreciable quantity of ruthenium distilled from concentrated nitric acid, but that no ruthenium was eliminated from solutions containing nitric acid up to 40 per cent by volume. Under the conditions above mentioned, iridium, which may be taken as representing the remaining members of the platinum group, did not appear in the distillate, but remained as a soluble compound in the distilling flask.

From solutions of sodium osmate, the form in which osmium is obtained during solution of metallic material in fused alkaline reagents, it was found that the osmium was easily and completely eliminated on acidifying with nitric acid.

It may thus be seen that the method of separation chosen will depend upon the composition of the solution from which the osmium is to be distilled and also upon the presence or absence of ruthenium.

XVI. SUMMARY OF RESULTS OBTAINED

1. Osmium, when present as a chloride or bromide, can be quantitatively precipitated as a hydrated dioxide from boiling solutions having a pH range from 1.5 to 6.3.

2. The presence of alkali chloride or sulphate during precipitation of the hydrated dioxide introduces no error into the determination. The alkali salts can be completely removed from the precipitate by washing.

3. There is a marked tendency to deflagrate when the hydrated dioxide is heated, even in the presence of hydrogen, with accompanying mechanical loss of osmium. This tendency is entirely overcome if the precipitate is impregnated with ammonium chloride.

4. The best filtering device for hydrated osmium dioxide is the Munroe crucible, but carefully prepared asbestos filters can be used for accurate determinations.

5. Osmium, which has been reduced in hydrogen and cooled to room temperature in carbon dioxide, remains unattacked by the air for a surprisingly long time. No error is introduced when it is inconvenient to make weighings immediately.

6. Osmium, when originally present as bromoosmate or as alkaline osmate, can be easily and completely eliminated as osmium tetroxide from boiling solutions containing approximately 10 per cent of nitric acid by volume. That present as chloroosmate, while it can be eliminated completely if distillation be continued for a long time, is not readily removed even by boiling concentrated nitric acid. Osmium, present as chloroosmate, is quickly separated as the tetroxide, however, from concentrated sulphuric acid near the boiling point of the acid, while that present as bromoosmate remains for the most part in the sulphuric-acid solution. When a mixture of sulphuric and nitric acids is used, osmium is readily eliminated from either type of compound.

7. No ruthenium is eliminated from boiling solutions containing nitric acid up to 40 per cent by volume nor from concentrated sul-

phuric acid alone, but, it is separated gradually from concentrated sulphuric acid containing nitric acid. A small but appreciable quantity of ruthenium is eliminated by boiling concentrated nitric acid.

8. The four remaining members of the platinum group do not appear in the distillate under the conditions described.

9. A solution of 6 normal hydrochloric acid saturated with sulphur dioxide is a very suitable reagent for the quantitative recovery of distilled osmium tetroxide.

10. A slight error is introduced unless the evaporated absorbent solution is digested and evaporated with concentrated hydrochloric acid a sufficient number of times to insure complete decomposition of sulphite compounds of osmium.

11. The thiourea test for the detection of osmium, described by Chugaev and said by him to be sensitive to 1 part in 100,000, can be

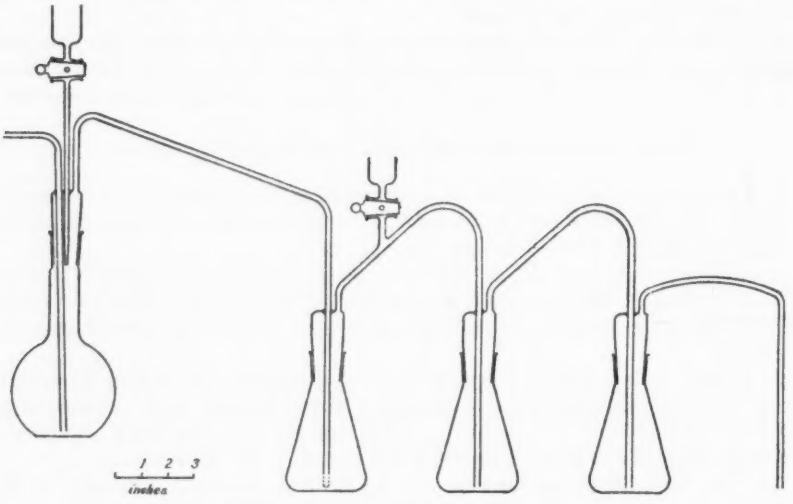

FIGURE 2.—*Distilling flask with train*

made much more sensitive: 0.02 mg of osmium in 100 ml (1 part in 5,000,000 parts of solution) can be detected. The test can be applied to solutions containing nitric acid if an excess of sulphur dioxide is first added.

XVII. METHOD OF ANALYSIS RECOMMENDED

The following procedure is designed to separate osmium as the volatile tetroxide from a solution containing the platinum group of metals; to recover the evolved tetroxide by absorption in 6 normal hydrochloric acid which has been saturated with sulphur dioxide; to precipitate the osmium as hydrated dioxide from the absorbent solution; and to obtain the osmium as metal.

1. DISTILLING APPARATUS

The distilling apparatus is shown in Figure 2. It consists of three main parts, namely, a 700 ml distilling flask, a set of three 300 ml

absorbing flasks, and a train of inlet and delivery tubes which are sealed into one rigid piece. The thistle tube closed by a stopcock, placed between the first and second absorbing flasks, serves to replenish the absorbing solution if an unusual amount of nitric acid is distilled and also, at the end of the distillation, to rinse the tube connecting the two flasks. The entire apparatus is constructed of pyrex glass. The joints must be very carefully ground, and are preferably uniform so that the flasks are interchangeable. It is important to note that these joints are sealed with a film of water only and not with lubricating grease, because the latter causes reduction of some osmium tetroxide to dioxide, which can not be readily recovered. It was found necessary to grease the stopcock in the tube used for the introduction of nitric acid into the distilling flask, but this constitutes the only exception. During operation, this delivery tube is frequently flushed with water to remove any osmium tetroxide which may have diffused into it. The diameter of this tube should be such that a column of water will be held. Three absorbing flasks are used but the absorption of osmium tetroxide is practically complete in the first flask and no osmium escapes the second flask.

2. PROCEDURE

Place 150 ml of 6 normal hydrochloric acid, which has been freshly saturated with sulphur dioxide, in the first absorbing flask and 50 ml of the same reagent solution in each of the other two flasks. Place the solution containing the osmium in the distilling flask and make sure that the separate parts of the entire apparatus are properly connected. If necessary, dilute the solution in the distilling flask to about 100 ml with water and add through the inlet tube 40 ml of nitric acid (1 volume of acid, specific gravity 1.42, diluted with 1 volume of water). Flush the thistle tube and stopcock with 10 ml of water. Pass a slow current of air through the apparatus and heat the solution in the distilling flask to boiling. Continue the distillation for one hour. This length of time should be sufficient to insure complete elimination of osmium from solutions in which the osmium is originally present as alkaline osmate or as bromoosmate. If, however, the osmium is present as chloroosmate the time required will be from seven to eight hours. In this case it is preferable to distil from concentrated sulphuric acid, or, if ruthenium is known to be absent, from concentrated sulphuric acid to which a few milliliters of nitric acid is added. Unite the portions of the absorbent solution and evaporate as far as possible on the steam bath in a clean unetched beaker. Digest the residue with 10 ml of hydrochloric acid (specific gravity 1.18) for 15 minutes and evaporate a second time. Repeat the digestion with hydrochloric acid and the evaporation three times more. This is done to insure complete decomposition of any sulphite compounds of osmium. Take up the residue from the last evaporation with 150 ml of water and heat to boiling. Add a solution of sodium bicarbonate, free from insoluble matter, until a precipitate appears and suddenly coagulates. Add a few drops of brom phenol blue indicator. Then add sufficient bicarbonate solution to produce a faint bluish color and boil five to six minutes.

Filter through a Munroe crucible, carefully pouring the supernatant liquid through first. Transfer the precipitate and wipe the

inner walls of the beaker and also the glass rod with a rubber policeman which has been well wetted. Wash thoroughly with a hot 1 per cent solution of ammonium chloride. Cover the precipitate with solid ammonium chloride. Moisten the ammonium chloride with a few drops of the wash solution and saturate the precipitate by suction. If desired, a saturated solution of ammonium chloride may be used to impregnate the precipitate. Continue the suction until the bottom of the crucible is coated with solidified ammonium chloride.

Wipe off this coating of salt and place the platinum cap on the bottom of the crucible. Cover the crucible with a Rose lid, preferably of quartz. Ignite a stream of hydrogen from a Rose delivery tube, likewise of quartz, and regulate the stream so that a very small flame is produced. Then insert the Rose tube through the opening in the Rose lid. The hydrogen flame will probably become extinguished by this operation and must be reignited. This is done by momentarily placing a burner flame under the crucible. The hydrogen will now burn as it issues from under the lid at the edge of the crucible. After five minutes gradually heat the crucible until all ammonium chloride is expelled. Ignite the osmium residue strongly in hydrogen for 10 minutes. Remove the burner and allow the crucible to cool somewhat. Extinguish the hydrogen flame by momentarily breaking the current of hydrogen and allow the crucible to cool to room temperature. Finally displace the hydrogen with a current of carbon dioxide and weigh as metallic osmium.

XVIII. ACKNOWLEDGMENTS

Asknowledgment is made to Edward Wichers for many helpful suggestions. The writer wishes also to express his appreciation to E. W. Zimmerman for the sketches of the apparatus shown.

WASHINGTON, January 21, 1931.

APPLICATION OF THE FLUORATING PROCESS TO FRUCTOSE

By D. H. Brauns and Harriet L. Frush

ABSTRACT

The prolonged action of hydrofluoric acid on fructose acetate involves both the reducing carbon (the second) and the first carbon, which is not asymmetric; whereas, former work has shown that for cellobiose acetate it involves both the reducing carbon (the first) and the second carbon, which is asymmetric and is reversed by this action. The prolonged action of hydrofluoric acid on fructose acetate is similar to the action of phenylhydrazine on fructose, which also spreads from the second to the first carbon. It seems probable that the nonasymmetry of the carbon is essential for explaining this behavior.

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I. INTRODUCTION

Previous investigation has shown that *brief* action of water-free hydrofluoric acid on acetylated sugars yields mono-fluor derivatives in which the acetyl group of the reducing carbon is replaced by fluorine. Thus crystalline fluoro derivatives of acetylated arabinose, xylose, glucose, fructose, cellobiose, gentiobiose, melibiose, and maltose have been prepared.[1]

Prolonged action of hydrofluoric acid on cellobiose octa-acetate caused a peculiar change, as not only the acetyl group of the reducing carbon was replaced by fluorine, but the acetyl group of the next carbon was split off and the resulting OH group reversed. A derivative of another sugar was formed, fluor-hexa-acetyl glucosido-mannose.[2]

II. PROLONGED ACTION OF HYDROFLUORIC ACID ON ACETYLATED FRUCTOSE

The present communication deals with the prolonged action of hydrofluoric acid on acetylated fructose. A crystalline compound [3]

[1] D. H. Brauns, J. Am. Chem. Soc., **45**, pp. 833, 2388; 1923; **46**, p. 1485; 1924; **49**, p. 3173; 1927; **51**, p. 1826; 1929. The series on optical rotation and atomic dimension will be continued separately.
[2] D. H. Brauns, J. Am. Chem. Soc., **48**, p. 2785; 1926.
[3] This compound has been prepared in small amount before (J. Am. Chem. Soc., **48**, p. 2780; 1926), but not investigated.

was separated, which was found by analysis to be a fluor-triacetyl hexose, one acetyl group being saponified (just as in cellobiose acetate) by the prolonged action of hydrofluoric acid. In this case, however, no reversion of an asymmetric group had occurred (as in the cellobiose derivative), since fluor-tetra-acetyl fructose was obtained on reacetylating, and was identified by the constants described for that compound.[4] We have further found, as described in detail below, that it is the acetyl group of the first or nonasymmetric carbon atom which has been saponified; hence, a reversion could not take place.

This difference in behavior of fructose and cellobiose may be explained in the following manner: In the case of fructose there are two dissimilar carbon atoms attached to the reducing carbon. One of these (the third) is asymmetric, but the other (the first) is not. Assuming that the groups attached to an asymmetric carbon have a more rigid configuration than those of a nonasymmetric carbon,[5] it will be found plausible that in case the arrangement of the asymmetric groups is not favorable a preference would exist for the nonasymmetric group. This spreading of a reaction to the first (nonasymmetric) carbon for fructose does not stand alone. It is similar to the action of phenylhydrazine on fructose yielding fructose (glucose) phenylosazone with fructose phenylhydrazone as an intermediate.

The following experimental results proved that the acetyl group of the first carbon was split off. The fluor-triacetyl fructose, which will be designated fluor-triacetyl fructose I, was methylated, yielding a new crystalline fructose derivative, fluor-methyl-triacetyl fructose I. The position of the methoxyl group in this compound was established as follows: The fluor-methyl triacetyl fructose I was saponified with barium hydroxide in the cold, by which not only the acetyl group, but also the fluorine atom was split off,[6] yielding a monomethyl fructose. This compound could not be obtained in crystalline form. A methoxyl determination showed the sirup to be a monomethyl fructose, and it did not give a phenylosazone under conditions which give for fructose an osazone with good yield. Of the two methyl fructoses (*1*-methyl and *2*-methyl) which obviously could not form an osazone,[7] only *1*-methyl fructose is possible here (since fluorine was attached to carbon 2 when fluor-triacetyl fructose was methylated). We conclude, therefore, that the compounds under investigation have the constitution *1*-methyl-*2*-fluor-triacetyl fructose and *1*-unsubs.-*2*-fluor-triacetyl fructose.[8]

Since it was suspected at first that the acetyl group of the third carbon had been saponified during prolonged fluoration, an attempt was made to prepare fluor-methyl-triacetyl fructose I, using *3*-methyl fructose [9] as the starting product.

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[4] See footnote 1, p. 449.

[5] There are at least two identical atoms or groups of atoms attached to a nonasymmetric carbon. This identity would make a deformation of the tetrahedral orientation of the valences easier than for an asymmetric carbon where tension must exist by the interference of the affinities of the four different atoms or groups.

[6] Exceptional behavior on the part of fructose. See experimental part.

[7] The figures indicate the carbon atom. *2*-Methyl fructose would, therefore, be identical with methyl fructoside. Irvine and Hynd (J. Chem. Soc., **95**, p. 1224; 1909) easily obtained a crystalline methyl fructose osazone from *3*-methyl fructose, which preparation they recommend for the identification of *3*-methyl fructose.

[8] "*1*-Unsubs." means that the hydroxyl group of the first carbon atom has not been replaced.

[9] Concerning the constitution of *3*-methyl fructose and α- and β-diacetone fructose, see Anderson, Charlton, Haworth, and Nicholson, J. Chem. Soc., p. 1337; 1929.

3-Methyl fructose was prepared according to the methods of Irvine and Hynd [10] and Ohle and Koller,[11] following the procedure: Fructose ——→*α*-diacetone fructose ——→*3*-methyl-diacetone fructose ——→*3*-methyl fructose.

The *3*-methyl fructose was acetylated with acetic anhydride and zinc chloride in the cold, yielding a new crystalline fructose derivative, *2*-unsubs-*3*-methyl-triacetyl fructose.[12] This compound was fluorated, giving the new crystalline derivative, *2*-fluor-*3*-methyl-triacetyl fructose, or fluor-methyl triacetyl fructose II. The melting points and specific rotations in chloroform of the two similar compounds are compared below:

Fluor-methyl-triacetyl fructose I, m. p. 94°, $[\alpha]_D^{20} = -116.30$.
Fluor-methyl-triacetyl fructose II, m. p. 113–114°, $[\alpha]_D^{20} = -88.70$.

It follows from the quoted constants that the two fluor-methyl-triacetyl fructose derivatives are not identical. This is due to the fact [13] (later established by the saponification with barium hydroxide), that the methoxyl group in fluor-methyl triacetyl fructose I is situated at carbon 1, whereas in fluor-methyl triacetyl fructose II it is at carbon 3.

Table 1 gives the specific and molecular rotations in chloroform of the four new fructose derivatives. The rotations in chloroform of *α*-diacetone fructose and its methyl derivative, which are included in Table 1, have not been recorded previously in the literature.

TABLE 1.—*Specific and molecular rotations of investigated compounds*

	Molecular weight	Specific rotation	Molecular rotation
1-Unsubs.-*2*-fluor-triacetyl fructose	308	−128.8	−396.7
1-Methyl-*2*-fluor-triacetyl fructose	322	−116.3	−374.5
α-Diacetone fructose	260	−146.6	−381.2
3-Methyl-diacetone fructose	274	−134.7	−369.1
2-Unsubs.-*3*-methyl-triacetyl fructose [1]	320	−84.1	−269.1
2-Fluor-*3*-methyl-triacetyl fructose	322	−88.7	−285.6

[1] It is obvious that *2*-unsubs.-*3*-methyl triacetyl fructose would be an excellent starting material for the preparation of a number of new compounds, such as *α*- and *β*-*3*-methyl tetra-acetyl fructose, *2*-*3* dimethyl triacetyl fructose and *2*-*3* dimethyl fructose. The methods have been described for the preparation of the analogous compounds: *α*- and *β*-penta-acetyl fructose, *β*-methyl tetra-acetyl fructose, and *β*-methyl fructose (C. S. Hudson and D. H. Brauns, J. Am. Chem. Soc., **37**; p. 2736; 1915; **38**; p. 1216; 1916.

III. EXPERIMENTAL

General remarks.—The saccharimeter degrees (S) are converted to circular degrees by multiplication by the factor 0.3462. Unless otherwise stated, volume of flask = 24.9784, length of tube = 4 dm.

1. 1-UNSUBS.-2-FLUOR-TRIACETYL FRUCTOSE

This compound may be prepared from *β*-penta-acetyl or *β*-tetra-acetyl fructose by the prolonged action of hydrofluoric acid. How-

[10] Irvine and Hynd, J. Chem. Soc., **95**; p. 1224; 1909.
[11] Ohle and Koller, Ber., **57**; p. 1571; 1924.
[12] Since fluorine attacks the reducing carbon first, and during the fluoration of this compound none of the acetyl groups was found to be removed, it follows that the hydroxyl group in *3*-methyl-triacetyl fructose must be on the second carbon atom. The ring structure of the newly described derivative is probably the same as that of tetra-acetyl fructose, since the method of acetylation of *3*-methyl fructose and of fructose is exactly the same. However, the particular ring structure of the compounds is not given as it does not affect the conclusions drawn.
[13] Concerning different ring structures, see footnote 12.

ever, since the yield is small and fluor-tetra-acetyl fructose is formed as an intermediate, it is advantageous to use the latter compound as a starting product. The receiver of the hydrofluoric acid still contained 15 g of powdered fluor-tetra-acetyl fructose and was cooled in ice and salt. After about 30 g of water-free hydrofluoric acid had been distilled, the receiver was well stoppered and immersed in brine, the temperature of which was allowed to rise gradually from $-11°$ to $-7°$ during a period of 26 hours. The receiver and brine were contained in a 1-gallon thermos jar which was kept in the refrigerator. These conditions were found the most advantageous for obtaining a maximum yield. The reaction product was worked up as previously described [14] and gave a light yellow sirup. Ether was added, the product evaporated to dryness, more ether added, and the mixture kept at 0° for 12 hours or more before filtering. The yield by this method was better and the product more nearly pure than when the mixture was filtered immediately and at room temperature. The compound was recrystallized four times from ether. The yield of pure substance was 10 per cent.

Rotation.—Second recrystallization: Subs., 0.5547; $\alpha = -32.65$ S; volume of flask, 24.9767 cc; $[\alpha]_D^{20} = -127.24$. *Third recrystallization:* Subs., 0.6024; 0.6131; $\alpha = -35.85$ S; -36.50 S; $[\alpha]_D^{20} = -128.66$; -128.70. *Fourth recrystallization:* Subs., 0.6175; $\alpha = -36.80$ S; volume of flask, 24.9784 cc; $[\alpha]_D^{20} = -128.83$. The specific rotation of the pure substance is taken as -128.8. The pure product crystallizes in well-defined prisms, is stable, colorless, and has a bitter taste. It is very soluble in most solvents except water, benzene, and petroleum ether. M. P. 134° to 135°. *Analyses*: Subs., 0.1881; CO_2, 0.3243; H_2O, 0.0937. Subs., 1.0135: CaF_2, 0.1190. Acetyl determination: Subs., 0.5000: 86.53 cc of 0.25 *N* H_2SO_4, 282.14 cc of 0.1 *N* NaOH. Molecular weight: Subs., 0.0816, 0.0855, 0.0048: Camphor, 0.1000. ΔT, 10.5°, 12.0°, 6.0°. *Calculated* for $C_6H_7O(C_2H_3O_2)_3$ OH F: C, 46.73; H, 5.56; F, 6.16; 64.9 cc of 0.1 *N* NaOH for AcOH + F; mol. wt., 308. *Found*: C, 47.02; H, 5.57; F, 5.71; 65.8 cc of 0.1 *N* NaOH; mol. wt., 311, 285, 319.

2. CONVERSION OF 1-UNSUBS.-2-FLUOR-TRIACETYL FRUCTOSE TO 2-FLUOR-TETRA-ACETYL FRUCTOSE

This conversion is important for proving that the prolonged fluoration has not reversed an asymmetric center in the molecule or caused any other change which would destroy the fructose structure.

One gram of powdered fluor-triacetyl fructose was added to a hot solution of 0.5 g of anhydrous sodium acetate in 8 cc of acetic anhydride and the mixture boiled for 10 minutes. The reaction product was poured into 100 cc of ice water and soon solidified to crystalline mass. It was separated on a suction filter and recrystallized from methyl alcohol. The determination of the specific rotation in chloroform gave the following results: *Rotation:* Subs., 0.5717; $\alpha = -24.20$ S; $[\alpha]_D^{20} = -91.60$. After recrystallization from ether the following results were obtained: Subs., 0.4075; $\alpha = -17.10$ S; $[\alpha]_D^{20} = -90.72$; m. p., 112°. When mixed with pure fluoro-tetra-acetyl fructose ($[\alpha]_D^{20} = -90.43$ in chloroform), the melting point was likewise 112°. These experiments prove that the prepared fluor-triacetyl compound is a fructose derivative.

[14] See footnote 1, p. 449.

3. 1-METHYL-2-FLUOR-TRIACETYL FRUCTOSE FROM 1-UNSUBS.-2-FLUOR-TRIACETYL FRUCTOSE

Two grams of powdered and dried fluor-triacetyl fructose was boiled for about five hours under reflux with 25 cc of methyl iodide, and 12 g of silver oxide was added gradually. The reaction product was diluted with ether, filtered by suction, and the precipitate washed with ether. The filtrate was evaporated in air and gave about 1.9 g of sirup, which solidified after being kept in a vacuum desiccator for two days and stirred with petroleum ether. The 1.7 g of impure crystals were dissolved in 1.5 liters of petroleum ether (b. p. 30° to 55°), filtered, and the filtrate allowed to evaporate in a beaker in air. As evaporation progressed the solution was transferred to smaller and smaller beakers. Impure crystals separated at the top, and were kept separate from those of the bottom and the lower part of the walls. Further recrystallizations were performed by allowing ether solutions to evaporate in air. The crystals were washed with 50 per cent ether-petroleum ether. The determination of the specific rotation in chloroform solution gave the following results: Subs., 0.6021: $\alpha = -29.50$ S; volume of flask, 24.9767 cc; $[\alpha]_D^{20} = -105.91$. *First recrystallization:* Subs., 0.5436: $\alpha = -28.65$ S; volume of flask, 24.9767; $[\alpha]_D^{20} = -113.90$. *Second recrystallization:* Subs., 0.4332: $\alpha = -23.30$ S; volume of flask, 24.9767 cc; $[\alpha]_D^{20} = -116.26$. *Third recrystallization:* Subs., 0.3950: $\alpha = -25.25$ S; volume of flask, 24.9767; $[\alpha]_D^{20} = -116.30$. The specific rotation of the pure substance is taken as -116.3; m. p., 94°. The pure product crystallizes in short prisms or plates and is very soluble in the ordinary solvents except water and petroleum ether. *Analyses*: Subs., 0.1894: CO_2, 0.3377; H_2O, 0.1029; OCH_3 determination: Subs., 0.2200: AgI, 0.1623. Acetyl determination: Subs., 0.4563: 96.49 cc of 0.25 *N* H_2SO_4, 296.79 cc of 0.1 *N* NaOH. *Calculated* for $C_6H_7O(C_2H_3O_2)OCH_3F$: C, 48.42; H, 5.94; OCH_3, 9.63; 56.64 cc of 0.1 *N* NaOH for AcOH + F. *Found:* C, 48.63; H, 6.08; OCH_3, 9.75; 55.57 cc of 0.1 *N* NaOH. A positive qualitative test for fluorine was obtained.

4. SAPONIFICATION OF 1-METHYL-2-FLUOR-TRIACETYL FRUCTOSE AND PROOF OF THE POSITION OF THE METHYL GROUP

One and three-fourths grams of crystalline barium hydroxide was dissolved in 25 cc of water on the steam bath and filtered into an Ehrlenmeyer flask with glass stopper. The solution was cooled with ice to about 5°, and 0.5 g of powdered methyl fluor-triacetyl fructose was added and shaken until dissolved. The solution was kept 1 hour longer in ice, then saturated with carbon dioxide and filtered. Sulphuric acid (0.25 *N*) was added until all barium was precipitated, but care was taken not to add an excess of the acid. Filtration was performed through a Gooch filter and the solution concentrated in vacuo. By dissolving in methyl alcohol, filtering, and evaporating, a thick, slightly yellowish sirup was obtained which was kept in a vacuum desiccator. A qualitative test for fluorine was negative.[15] A methoxyl determination proved the sirup to be a monomethyl fructose. OCH_3 determination: Subs., 0.1412: AgI, 0.1752.

[15] It is remarkable that this method of saponification does not affect the fluorine in fluor-acetyl derivatives of the aldoses, but removes it from this derivative of fructose, and also from fluor-tetra-acetyl fructose.

Found: OCH_3, 16.4 per cent. *Calculated* for $C_6H_{11}O_5$ (OCH_3), 15.98 per cent.

The following experiment proves that the monomethyl fructose does not form an osazone:

Thirty milligrams of the sirup obtained from the described saponification was dissolved in 3 cc of water. A solution of 0.4 g of freshly prepared phenylhydrazine in 0.3 cc of acetic acid and 3 cc of water was added, and the resulting solution heated in a steam bath. The heating was continued for 45 minutes but no crystals separated even on cooling the solution. Thirty milligrams of fructose when treated in the same manner gave a nearly quantitative yield of pure osazone.

5. 3-METHYL TRIACETYL FRUCTOSE

α-Diacetone fructose (*1-2, 4-5* diacetone fructose) was prepared according to the method of Ohle and Koller.[16] The specific rotation of the chloroform solution gave the following results: *Second recrystallization:* Subs., 0.5685: $\alpha = -38.40$ S; $[\alpha]_D^{20} = -146.70$. *Third recrystallization:* Subs., 0.5373: $\alpha = -36.43$; $[\alpha]_D^{20} = -146.57$. *Fourth recrystallization:* Subs., 0.5767: $\alpha = -39.10$ S; $[\alpha]_D^{20} = -146.57$. The specific rotation of the pure substance in chloroform is taken as -146.6; m. p., 118° to 119° (Fischer, 119° to 120°).

The specific rotation of the pure substance in water was -160.5 (Fischer, $[\alpha]_D^{20} = -161.3$ in water).

3-Methyl diacetone fructose was prepared according to Irvine and Hynd.[17] We did not have the difficulties which these authors report in obtaining a good yield of pure product (50 per cent) if amounts larger than 10 g of α-diacetone fructose were worked with at one time. We have methylated quantities of 35 g and 45 g of fructose diacetone and obtained 52 per cent yield of pure *3*-methyl-diacetone fructose. It may be that the silver oxide which we dried at 80° in a vacuum of less than 1 mm of mercury was more active than that used by Irvine and Hynd.

The substance was recrystallized from dilute methyl alcohol (3 alcohol : 1 water). The determination of the specific rotation in chloroform gave the following results: *First crystallization* of the crude product of $[\alpha]_D^{20} = -136.0$. Subs., 0.5023, 0.5896: $\alpha = -31.25$ S, -36.75 S; $[\alpha]_D^{20} = -134.52$, -134.75. *Second recrystallization:* Subs., 0.6173, 0.6547: $\alpha = -38.45$ S, -40.80 S; $[\alpha]_D^{20} = -134.65$, -134.73. The specific rotation in chloroform is taken as -134.7. Our values for the specific rotation of the pure substance in acetone, and the melting point (115°) agree with those obtained by Irvine and Hynd.

The method of Irvine and Hynd [18] was followed by hydrolyzing *3*-methyl diacetone fructose with 0.1 per cent hydrochloric acid. However, a product was obtained which was only partially hydrolyzed, as was found by methoxyl content and specific rotation. Twice the strength of the acid (0.2 per cent HCl) gave complete hydrolysis of the acetone groups. The *3*-methyl fructose was recrystallized from ethyl acetate containing about 5 per cent methyl alcohol.

3-methyl triacetyl fructose was prepared from *3*-methyl fructose by the same method used for the preparation of tetra-acetyl fructose

[16] See footnote 11, p. 451.
[17] See footnote 10, p. 451.
[18] See footnote 10, p. 451.

from fructose. Four grams of finely powdered *3*-methyl fructose was added gradually to a cold solution of 0.35 g. of zinc chloride in 20 cc. of acetic anhydride. The mixture was cooled in ice and vigorously shaken until only a small part of the *3*-methyl fructose remained undissolved (about 30 minutes). The cold solution was then poured into 30 cc. of ice water in a flat porcelain dish, 20 g. of sodium bicarbonate was added and the mixture allowed to stand for 30 minutes. The excess of sodium bicarbonate was filtered off by suction and washed with chloroform. The filtrate was shaken out with chloroform, the chloroform solution dried with sodium sulfate, and evaporated in a current of air. The crystals which separated were stirred with ether, and filtered off by suction. The crude product (0.9 g.) was recrystallized from ether containing a little absolute alcohol. Yield of pure substance, 20 per cent. In working up larger amounts than 4 g. of *3*-methyl fructose, the yield became relatively smaller. *Rotation:* Subs., 0.6182: $\alpha = -23.05$ S; $[\alpha]_D^{20} = -80.61$. *First recrystallization:* Subs., 0.6237: $\alpha = -24.25$ S; $[\alpha]_D^{20} = -84.05$. *Second, recrystallization:* Subs., 0.5989: $\alpha = -23.30$ S; $[\alpha]_D^{20} = -84.11$. The specific rotation of the pure substance in chloroform is taken as -84.1. The compound crystallizes in needles and is bitter; m. p., 156–157°. It is stable and soluble in ordinary solvents, fairly soluble in ether and slightly in water and petroleum ether. *Analyses:* Subs., 0.2102: CO_2, 0.3765; H_2O, 0.1188. OCH_3 determination: Subs., 0.2091: AgI, 0.1546. Acetyl determination: Subs., 0.5012: 96.49 cc. of 0.25 H_2SO_4, 287.99 cc. of 0.1 *N* NaOH. *Calculated* for $C_6H_8O_2(C_2H_3O_2)_3$ OCH_3: C, 48.72; H, 6.30; OCH_3, 9.70; AcOH. 56.25. *Found:* C, 48.85; H, 6.32; OCH_3, 9.78; AcOH, 56.02.

6. 2-FLUOR-3-METHYL TRIACETYL FRUCTOSE

The method of fluorating *3*-methyl triacetyl fructose is the same as described for fluorating the acetylated sugars.[19] The receiver contained 4 g. of powdered *3*-methyl triacetyl fructose and the still about 40 g. of potassium bifluoride. The distillation was finished in about 45 minutes and the reaction product was worked up directly. After evaporation of the chloroform, the residue crystallized when stirred with ether. The yield of crude product separated by suction was 2.7 g. Upon recrystallization from ether two fractions were obtained; one contained fluorine, the other did not. They differed considerably in melting point and specific rotation. The fluor-containing compound was recrystallized until a constant specific rotation (in chloroform) was reached. The amount of the other compound (which probably was not the original methyl-triacetyl fructose) was too small for purification. *Rotation:* First recrystallization: Subs., 0.5861: $\alpha = -24.15$ S; $[\alpha]_D^{20} = -89.08$. Second recrystallization, first, second, and third fraction, respectively: Subs., 0.5996, 0.5711, 0.4080: $\alpha = -24.60$ S, -23.40 S, -16.75 S; $[\alpha]_D^{20} = -88.70, -88.57, -88.75$. The specific rotation of the pure substance in chloroform was taken as -88.7; m. p., 113° to 114°. The pure substance crystallizes in needles or small prisms and has a bitter taste. It is very soluble in ordinary solvents except petroleum ether and water. *Analyses:* Subs., 0.2099: CO_2, 0.3717; H_2O, 0.1120.

[19] See footnote 1, p. 449.

Subs., 0.5000: CaF_2, 0.0525. OCH_3 determination: Subs., 0.2008: AgI, 0.1499. *Acetyl determination:* Subs., 0.5008: 96.08 cc. of 0.25 *N* H_2SO_4, 302.35 cc. of 0.1 *N* NaOH. *Calculated* for $C_6H_7O.F.OCH_3(C_2H_3O_2)_3$: C, 48.42; H, 5.94; F, 5.90; OCH_3, 9.63; 62.16 cc. of 0.1 *N* NaOH for AcOH+F. *Found:* C, 48.30; H, 5.97; F, 5.12; OCH_3, 9.87; 62.15 cc. of 0.1 *N* NaOH.

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MOISTURE EXPANSION OF GLAZES AND OTHER CERAMIC FINISHES

By H. G. Schurecht and G. R. Pole[1]

ABSTRACT

Research for ascertaining why some glazes are more resistant to "moisture crazing" than others revealed the fact that certain glazes expand, because of the action of water, similarly to some of the ceramic bodies to which they are applied. Although a control of this type of expansion is very important in fitting glazes to bodies, it has not been previously considered. Its importance should be evident at once when it is considered that a large "moisture expansion" in a glaze, or other finish, is in many cases an indication that the glaze will not be so liable to craze when the ceramic ware of material on which it is used is exposed to moisture. This follows since the glaze and the body on which it goes and which is ordinarily very susceptible to this kind of expansion will then increase in size simultaneously and more nearly at the same rate. Such conditions lessen the tendency of the body expansion to cause tensile stresses in the glaze.

In this investigation specimens of various finishes were subjected to steam at 150 lbs./in.^{2} for an hour because it was known that this treatment of such materials produces similar effects to those caused by long exposure to weather. This artificial weathering treatment caused in lustrous glazes an average expansion of 0.004 per cent, in mat glazes 0.011 per cent, in vitreous slip finishes 0.005 per cent, and in porous slip finishes 0.033 per cent. The moisture expansion of one of the mat glazes was 30 per cent of the average obtained for a ceramic body having an absorption of approximately 12 per cent. This proclivity of ceramic finishes to expand by the absorption of moisture can be controlled in their manufacture.

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I. INTRODUCTION

It has been shown [2] that a type of delayed crazing found on glazed ceramic ware may, in certain cases, be caused by a gradual expansion produced by the action of moisture on the body during storage or use. It has also been demonstrated that by subjecting glazed bodies to steam at a pressure of 150 lbs./in.^{2} some of the effects produced are very similar to those obtained by exposure to weather. Moreover it was found [3] that this type of crazing may be prevented by adjusting the relative expansivity of the glaze with respect to the body so that the glaze is under a fairly high compression when the ware is removed from the kiln.

[1] Research associates of the National Terra Cotta Society at the National Bureau of Standards.
[2] Methods for Testing Crazing of Glazes Caused by Increases in Size of Ceramic Bodies, J. Am. Cer. Soc., **11**, pp. 271–277; 1928.
[3] Effect of Water on Expansions of Ceramic Bodies of Different Compositions, B. S. Jour., Research, **3**, pp. 331–341; 1929; J. Am. Ceram. Soc., **12**, pp. 596–604; 1929.

Preliminary studies indicated, however, that some of the porous slip finishes or engobes develop a "moisture expansion" similar in magnitude to that obtained in the body on which they go, and, hence, that it is unnecessary to have such finishes in high compression in order to prevent "moisture crazing." It was also found that some glazes may be in less compression than others to prevent such crazing. This led to the belief that these glazes as well as the engobes develop a moisture expansion. The investigation was, therefore, continued to test this opinion, and the results to date evidently confirm it.

II. EXPERIMENTAL METHODS

Four different lustrous glazes, 5 mat glazes, 5 porous slip finishes, and 2 vitreous slip finishes were studied in this investigation. In one portion of the tests, bars of the glazes and other ceramic finishes, approximately 1 by 1 by 6 inches in size, were used as specimens. These bars were made by filling fire-clay troughs with the raw glazes, or engobes, and firing them to the regular maturing temperatures of the finishes. These temperatures ranged from cones 3 to 6. After firing, the fire-clay troughs were ground from the fused bars of glazes and engobes. Pyrex glass capillary reference tubes were then cemented in grooves which had been cut about 5 inches apart in the bars. The distances between these tubes were measured by means of a microscope comparator [4] and the bars were then subjected to steam at a pressure of 150 lbs./in.^{2} in an autoclave for one hour. After this treatment the specimens were cooled and the distances between the reference marks remeasured in order to determine the expansions produced. The specimens were then subjected to steam at a pressure of 300 lbs./in.^{2} for another hour to determine the additional expansion caused by this more severe treatment.

In another test, the same finishes were applied to the outside surfaces only of cylindrical rings having 2-inch outside diameters as described in a previous article.[5] Each finish was tested on rings of the same bodies for which it was developed by the manufacturer. Two reference marks consisting of thin capillary pyrex tubes cemented in holes approximately one-fourth inch apart were established on the upper edge of each ring. The rings were cut open between these reference marks whose distances apart were then measured with a micrometer microscope. After this, the rings were subjected to steam at a pressure of 75 lbs./in.^{2} for one hour in an autoclave and cooled for a remeasurement of the distances between the marks. The increases noted in these distances resulted because the effect of moisture, absorbed during the treatment, expanded the finishes less than it did the bodies of the rings. When different finishes are on rings having the same body these increases become larger, therefore, as the susceptibility of the finishes to moisture expansion decreases. The results obtained are given in Table 2, and represent in every case the average obtained on three duplicate specimens after corrections were made for any discrepancy occurring in the temperatures at which the measurements were made. The variations between the results obtained on duplicates were usually less than ± 0.001 cm.

[4] The comparator used in this work was designed by C. S. Laubly, of the National Bureau of Standards, and is described in Shrinkage of Portland Cement, by J. C. Pearson, Am. Concrete Inst.; 1921.

[5] Methods of Measuring Strains Between Glazes and Ceramic Bodies, B. S. Jour. Research, **5**, pp. 97-103; 1903; J. Am. Ceram. Soc., **13**, pp. 369-375; 1930.

To determine the degree to which these finishes are subject to crazing as a result of this differential moisture expansion between them and the bodies, crazing tests were carried out on 4 by 4 by 1 inch tile made of the appropriate bodies as in the case of the rings. In these tests the treatment was the same as in the ring tests except that a second treatment at a steam pressure of 150 lbs./in.^{2} was also given. The results are incorporated in Table 2.

III. RESULTS ON BARS OF CERAMIC FINISHES

The results obtained on the bars made of the glazes and other ceramic finishes are given in Table 1.

The lustrous glazes developed moisture expansions ranging between 0.001 and 0.009 per cent with an average of 0.004 per cent when treated with steam at a pressure of 150 lbs./in.^{2} for one hour. When treated with steam at a pressure of 300 lbs./in.^{2} for one hour subsequent to the 150-pound treatment, the total expansions resulting from the two treatments ranged between 0.002 and 0.012 per cent, with an average of 0.005 per cent.

The mat glazes expanded 0.003 to 0.015 per cent with an average of 0.010 per cent when treated with steam at a pressure of 150 lbs./in.^{2}; and on being subjected to the 300-pound treatment, the total expansions ranged between 0.003 and 0.030 per cent, with an average of 0.017 per cent.

The vitreous slip finishes developed moisture expansions ranging between 0.004 and 0.006 per cent, with an average of 0.005 per cent when treated with steam at 150 pounds; and when subsequently subjected to the 300-pound treatment the total expansions arising from the two treatments ranged between 0.022 and 0.029 per cent, with an average of 0.026 per cent.

The porous slip finishes expanded 0.020 to 0.067 per cent, with an average of 0.033 per cent as a result of the treatment at 150 pounds; when treated at 300 pounds the total expansions from the two treatments were between 0.029 and 0.139 per cent, with an average of 0.078 per cent.

In a previous work [6] some porous ceramic bodies were found to expand 0.055 to 0.125 per cent as a result of this treatment with steam at 150 pounds for an hour. In comparison, the expansion of one of the mat glazes mentioned above was 0.015 per cent when treated in this way; that is, the expansion of this glaze amounts to between 12.5 and 30 per cent of that developed in the porous ceramic bodies previously tested.

IV. RESULTS WITH CERAMIC FINISHES ON RINGS

The results shown in Table 2 and obtained with the glazes and other ceramic finishes when they were applied to rings made of the appropriate bodies have in part been plotted in Figures 1 and 2 against the corresponding results in Table 1. The values obtained by the ring method are too low when the finishes craze since some of the strain between the body and finish is relieved by this crazing; and for this reason some of the data are not included in the figures. It is

[6] "Methods for Testing Crazing of Glazes." Work cited, p. 274.

evident from the figures that, in general, those finishes which develop the least moisture expansion caused the rings made from a given body to expand the most when they were treated with steam at 75 lbs./in.^{2} for one hour, hence the reciprocals of the expansions of these rings may be used as qualitative indicators of the comparative degrees to which the moisture expansions of the glazes fall short of that of the body represented in the rings.

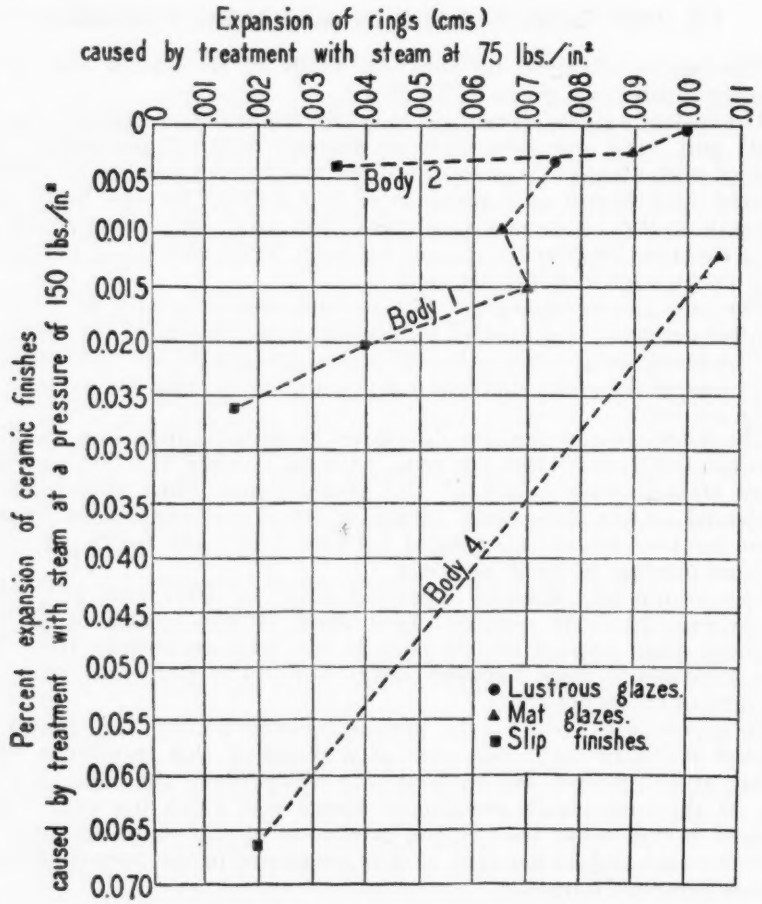

FIGURE 1.—*Comparison of the moisture expansions of ceramic finishes and expansions of rings with these finishes*

It must be remembered, however, that the expansion of the rings during an autoclave treatment is also governed to some extent by certain other physical properties of the finishes and bodies, such as, for example, the elasticity and tensile strength. These factors are always important and especially so where there is little or no moisture expansion in the finish to reduce the tensile stresses set up in it by the swelling of the body. Although the moisture expansion tests made

on rings are qualitative and not as accurate as tests made on bars of the finishes, the ring test has the advantage over the bar test in that its measurements are made on combinations of glaze and body prepared and treated under conditions almost exactly like those employed on the same combinations when they are prepared for actual use.

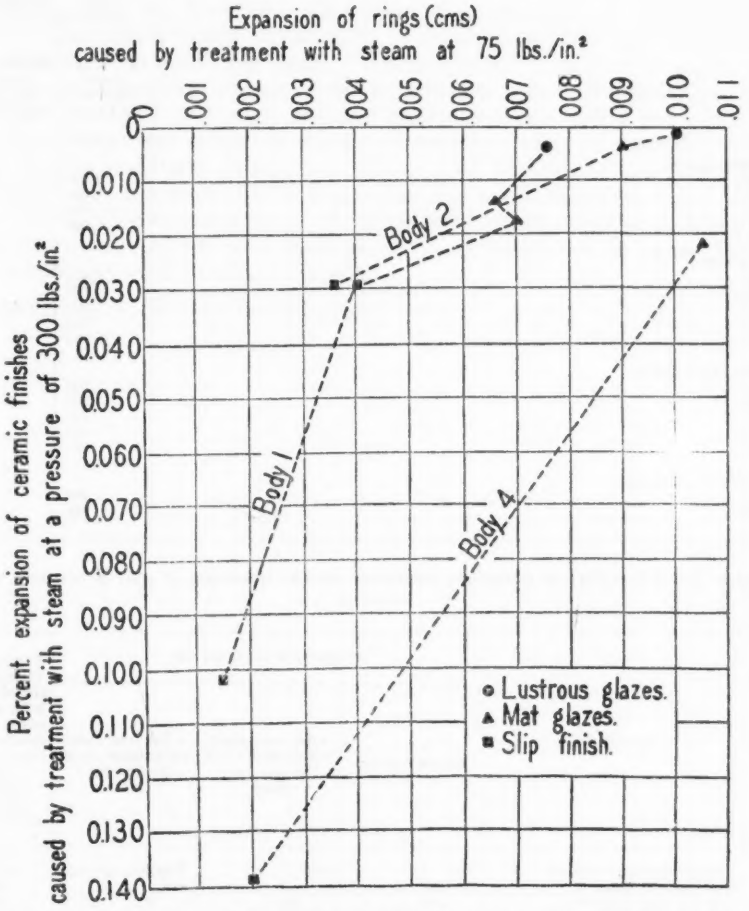

FIGURE 2.—*Comparison of the moisture expansions of ceramic finishes and expansions of rings with these finishes*

Furthermore, it can be conducted in less time and with less expensive apparatus than that required for the bar test. In employing the ring test to compare moisture expansions of glazes it is, of course, necessary to use the same ring body fired to the same temperature for all of the glazes.

TABLE 1.—*Moisture expansions of glazes and other ceramic finishes when subjected to an autoclave treatment*

	Expansions (in per cent) of bars made of glazes and other ceramic finishes. (Average of 3 tests. Variations = ±0.0005 per cent)	
	150 lbs./in.² steam pressure for 1 hour	300 lbs./in.² steam pressure for 1 hour
Lustrous glazes:		
A	0.003	0.004
B	.001	.002
C	.002	.005
D	.009	.012
Mat glazes:		
A	.015	.017
B	.009	.013
C	.003	.003
D	.013	.030
E	.012	.021
Porous slip finishes:		
A	.020	.029
B	.026	.102
C	.030	.070
D	.020	.048
E	.067	.139
Vitreous slip finishes:		
A	.004	.029
B	.006	.022

TABLE 2.—*The effect of autoclave treatment on the tendency of glazed ceramic ware to craze*

Body	Ceramic finish	Appearance of glazed tile			Expansion (in cm) of glazed rings from treatment with steam at 75 lbs./in.² for 1 hour. (Variation = ±0.001 cm)
		Before testing	After treatment with steam at 75 lbs./in.² for 1 hour	After treatment with steam at 150 lbs./in.² for 1 hour	
1	White lustrous glaze A	OK	OK	Medium crazing.	0.0075
	White mat glaze A	do	do	OK	.0070
	White mat glaze B	do	do	do	.0065
	Porous slip finish A	do	do	do	.0040
	Porous slip finish B	do	do	do	.0015
2	White lustrous glaze B	do	do	Badly crazed	.0100
	White mat glaze C	do	do	Slightly crazed	.0090
	Vitreous slip finish A	do	do	Badly crazed	.0035
3	White lustrous glaze on C	Slightly crazed	Badly crazed		[1] .0075+
	White mat glaze D	Medium crazing.	do		
	Vitreous slip finish B	OK	OK	OK	.0040
	Porous slip finish C	Medium crazing.	Badly crazed		.0015+
4	White lustrous glaze D	Slightly crazed	Slightly crazed		.0045+
	White mat glaze E	OK	OK	Badly crazed	.0105
	Porous slip finish D	Slightly crazed	Slightly crazed		.0090+
	Porous slip finish E	OK	OK	Slightly crazed	.0020

[1] The expansions of rings which were crazed are marked plus (+), since some of the strain between the body and slip has been relieved by crazing of the slip.

V. SUMMARY AND CONCLUSIONS

1. Some mat and lustrous glazes as well as slip finishes expand similarly to porous ceramic bodies from the action of water. This fact is of fundamental importance in fitting glazes to ceramic bodies.

2. In general, slip finishes develop the highest moisture expansions, and when they are treated with steam at a pressure of 150 lbs./in.^{2} for one hour the average expansion, as determined by this investigation, amounts to 0.033 per cent. When treated in a similar manner, the average expansion obtained for mat glazes was 0.011 per cent, for vitreous slip 0.005 per cent, and for lustrous glazes 0.004 per cent.

3. The ring test may be used advantageously to compare the approximate moisture expansions of ceramic finishes if the rings are all made from the same body treated in the same manner.

4. The moisture expansions of glazes and other ceramic finishes is often more important with respect to their tendency to craze than their elasticity and tensile strength.

WASHINGTON, September 8, 1930.

EXTENSION OF THE STANDARD VISIBILITY FUNCTION TO INTERVALS OF 1 MILLIMICRON BY THIRD-DIFFERENCE OSCULATORY INTERPOLATION

By Deane B. Judd

ABSTRACT

The two empiric representations (Tyndall-Gibson and Walsh) of the visibility of radiant energy yield curves which fail to pass exactly through the values at every 10 mμ adopted as standard; hence, they can not serve as means of obtaining interpolated values. By the method of osculatory interpolation the visibility function is represented as a series of parabolas of the third degree which join at the specified values so as to have a common first derivative at the junction point. The discontinuities in derivatives of higher order which exist at the junction points are sufficiently small to be of no consequence.

Since the adoption of the Gibson-Tyndall[1] recommended visibility function as the international standard[2] two empiric formulas have been proposed for its approximate representation, one by Tyndall and Gibson[3] and the other, which is of the same type, but with a somewhat better choice of constants, by Walsh.[4] Such empiric formulas as these have obvious uses;[5] and if a similar formula were at hand which fitted the adopted values of visibility exactly, it would be of somewhat more extended use than either of the formulas already proposed; for example, it would serve to yield interpolated values of perfect continuity possessing continuous derivatives of all orders. It is not to be supposed, of course, that interpolation by such a formula, or by any other method, graphical or mechanical, yields any information concerning the true course of the standard visibility function between the specified points. In fact, that course is wholly unspecified, and there are a large number of smooth curves to be drawn through these intervals. It has been found convenient in the work of the National Bureau of Standards to adopt arbitrarily a single one of these curves. The interpolated values adopted are found by a method superior to any graphical interpolation because the values may be reproduced at any time anywhere, and it is believed that this method is superior to solutions by other formulas for interpolation because it combines continuity in function and in first derivative with

[1] K. S. Gibson and E. P. T. Tyndall, The Visibility of Radiant Energy, B. S. Sci. Paper No. 475, p. 174; 1923.
[2] Proc. International Commission on Illumination, 6th meeting, Geneva, pp. 67 and 232; July, 1924.
[3] E. P. T. Tyndall and K. S. Gibson, Visibility of Radiant Energy Equation, J. Opt. Soc. Am. and Rev. Sci. Inst., 9, p. 403; 1924.
[4] J. W. T. Walsh, Visibility of Radiant Energy Equation, J. Opt. Soc. Am. and Rev. Sci. Inst., 11, pp. 111-112; 1925.
[5] For example, the Tyndall-Gibson formula was used by Ives in computing radiant luminous efficiency (H. E. Ives, The Luminous Properties of the Black Body, J. Opt. Soc. Am. and Rev. Sci. Inst., 12, pp. 75-78; 1926).

considerable computational convenience. Indeed, the ease of applying this method is so great that the labor involved differs little from that of the graphical method.

The method used is interpolation by the third-difference, osculatory formula developed by Karup.[6] Application of this formula, interval by interval, results in a series of parabolas of the third degree which join each other at the specified values of the function in such a way as to yield a continuous curve having a continuous first derivative; derivatives of higher order are discontinuous at the specified points to a greater or less degree according as differences of higher order than the second are great or small.[7] Although Karup presented a method of applying this formula by computing from the leading major differences (see, for example, Table 1) the leading minor differences (that is, the leading differences referring to the nine interpolated values), and then deriving the desired interpolated values by continuous addition, the present interpolation of the visibility function was performed by actually finding the products indicated in the formula and taking their sum. In this way it was found possible with the aid of a computing machine to obtain nine interpolated values and to check them by an independent method in about 15 minutes;[8] it seems doubtful whether the continuous addition method would be much more expeditious.

If V_λ be the visibility for wave length, λ, and $\Delta_1 V_{\lambda_o-10}$, $\Delta_2 V_{\lambda_o-10}$ and $\Delta_3 V_{\lambda_o-10}$ be, respectively, the first, second, and third leading major differences as exemplified in the first row of Table 1 for $\lambda_o = 550$ mμ, then we compute by the third-difference osculatory formula the interpolated values within the wave-length interval, λ_o to $\lambda_o + 10$, as:

$$V_\lambda = V_{\lambda_o-10} + K_1\Delta_1 V_{\lambda_o-10} + K_2\Delta_2 V_{\lambda_o-10} + K_3\Delta_3 V_{\lambda_o-10}$$

where:

$$K_1 = (\lambda - \lambda_o + 10)/10$$
$$K_2 = (\lambda - \lambda_o + 10)\ (\lambda - \lambda_o)/200$$
$$K_3 = (\lambda - \lambda_o)^2\ (\lambda - \lambda_o - 10)/2{,}000$$

Since we wish at present merely to extend the visibility function to values for every millimicron, it is necessary only to find by interpolation nine new values within each 10 mμ interval; hence the coefficients, K_1, K_2, and K_3, may be completely evaluated for this purpose by setting in succession $\lambda - \lambda_o$ equal to 1, 2, ... 9. Table 3 gives such values of the coefficients, K_1, K_2, and K_3. Table 4 gives the details of the computation for the wave-length interval,

[6] J. Karup, On a New Mechanical Method of Graduation, Trans. 2d Int. Actuarial Congress, p. 83; 1898. J. W. Glover, Derivation of the United States Mortality Table by Osculatory Interpolation, Quarterly Publications of the American Statistical Assoc., **12**, p. 90; 1910.

[7] The term, osculatory, applies with more aptness to interpolation by the fifth (and higher) difference formulas than to the third-difference formula because for these formulas the second derivative as well as the first is continuous at the specified values, which insures that the successive parabolas join so as to have a common osculating circle at the point of junction. The third-difference formula is also commonly referred to as an osculatory formula because Karup used that term and because it is derived by argument similar to that leading to the formulas involving fifth differences, or differences of higher order. We might have used the fifth-difference formula here, but since, due to the regularity of the standard visibility function, the resulting values would not differ appreciably from those by the third-difference formula, the added labor would not have resulted in any practical gain.

[8] The check was carried out by taking the differences in the ascending order rather than in the descending order as indicated by the formula. In general, the resulting products need not be found; they are discovered to be already evaluated incidental to the determination of interpolated values in descending order for other wave lengths; the check consists, therefore, of assembling in different groupings, for addition, products already found. (See Tables 1, 2 and 4.)

550 to 560 mμ, together with the check by the ascending differences whose computation is indicated in Table 2. The leading ascending differences, $\nabla_1 V_{\lambda_o+20}$, $\nabla_2 V_{\lambda_o+20}$ and $\nabla_3 V_{\lambda_o+20}$, for $\lambda_o = 550$ mμ, appear in the first row of the table.

The values of the visibility function obtained in this manner for every millimicron are given in Table 5, together with the values for every 10mμ (bold-face type) from which the interpolated values were computed.[9] The function defined, interval by interval, by the third-difference osculatory, interpolation formula is, as mentioned before, continuous and possesses a continuous first derivative. The derivatives of higher order, however, are not continuous through the specified points at every 10 mμ. Nevertheless, since no marked irregularities occur in the standard values of visibility, these discontinuities in derivatives of higher order are of small magnitude and may be neglected.

TABLE 1.—*Computation of the leading descending differences,* $\lambda_o = 550$ *mμ*

λ in mμ	V_λ	$\Delta_1 V_\lambda$	$\Delta_2 V_\lambda$	$\Delta_3 V_\lambda$
540	0.954	+0.041	−0.041	−0.002
550	.995	.000	−.043	
560	.995	−.043		
570	.952			

TABLE 2.—*Computation of the leading ascending differences,* $\lambda_o = 550$ *mμ*

λ in mμ	V_λ	$\nabla_1 V_\lambda$	$\nabla_2 V_\lambda$	$\nabla_3 V_\lambda$
570	0.952	+0.043	−0.043	+0.002
560	.995	.000	−.041	
550	.995	−.041		
540	.954			

TABLE 3.—*Coefficients,* K_1, K_2, *and* K_3, *for interpolation to tenths by the third-difference, osculatory, interpolation formula:*

$$V_\lambda = V_{\lambda_o-10} + K_1\Delta_1 V_{\lambda_o-10} + K_2\Delta_2 V_{\lambda_o-10} + K_3\Delta_3 V_{\lambda_o-10}$$

$\lambda-\lambda_o$	K_1	K_2	K_3
1	+1.1	+0.055	−0.0045
2	+1.2	+.120	−.0160
3	+1.3	+.195	−.0315
4	+1.4	+.280	−.0480
5	+1.5	+.375	−.0625
6	+1.6	+.480	−.0720
7	+1.7	+.595	−.0735
8	+1.8	+.720	−.0640
9	+1.9	+.855	−.0405

[9] The first and last intervals were filled in by assuming the visibility for this purpose to be 0.000012 and 0.000015 at 370 and 780 mμ, respectively.

TABLE 4.—*Example of interpolation of the visibility function by the third-difference, osculatory formula, descending differences; check by ascending differences*

For $\lambda_o = 550$ mμ we may write from Table 1:

$$V_\lambda = 0.954 + 0.041\ K_1 - 0.041\ K_2 - 0.002\ K_3$$

The coefficients, K_1, K_2, and K_3, may be found in Table 3

λ in mμ	$+0.041\ K_1$	$-0.041\ K_2$	$-0.002\ K_3$	V_λ
551	+0.045100	−0.002255	+0.000009	0.996854
552	+.049200	−.004920	+.000032	.998312
553	+.053300	−.007995	+.000063	.999368
554	+.057400	−.011480	+.000096	1.000016
555	+.061500	−.015375	+.000125	1.000250
556	+.065600	−.019680	+.000144	1.000064
557	+.069700	−.024395	+.000147	.999452
558	+.073800	−.029520	+.000128	.998408
559	+.077900	−.035055	+.000081	.996926

Check by ascending differences: From Table 2 we write:

$$V_\lambda = 0.952 + 0.043\ K_1' - 0.043\ K_2' + 0.002\ K_3'$$

The coefficients, K_1', K_2', and K_3', may be found in Table 3 by reading the values of the coefficients, K_1, K_2, and K_3, for $10 - \lambda + \lambda_o$.

λ in mμ	$+0.043\ K_1'$	$-0.043\ K_2'$	$+0.002\ K_3'$	V_λ
551	+0.081700	−0.036765	−0.000081	0.996854
552	+.077400	−.030960	−.000128	.998312
553	+.073100	−.025585	−.000147	.999368
554	+.068800	−.020640	−.000144	1.000016
555	+.064500	−.016125	−.000125	1.000250
556	+.060200	−.012040	−.000096	1.000064
557	+.055900	−.008385	−.000063	.999452
558	+.051600	−.005160	−.000032	.998408
559	+.047300	−.002365	−.000009	.996926

TABLE 5.—*The standard visibility function extended to values for every millimicron by third-difference osculatory interpolation*

λ in mμ	V_λ	λ in mμ	V_λ	λ in mμ	V_λ	λ in mμ	V_λ	λ in mμ	V_λ	λ in mμ	V_λ
380	**0.00004**	**450**	**0.038**	**520**	**0.710**	**590**	**0.757**	**660**	**0.061**	**730**	**0.00052**
1	.000045	1	.0399	1	.7277	1	.7449	1	.0574	1	.000482
2	.000049	2	.0418	2	.7449	2	.7327	2	.0539	2	.000447
3	.000054	3	.0438	3	.7615	3	.7202	3	.0506	3	.000415
4	.000059	4	.0459	4	.7776	4	.7076	4	.0475	4	.000387
5	.000064	5	.0480	5	.7932	5	.6949	5	.0446	5	.000360
6	.000071	6	.0502	6	.8082	6	.6822	6	.0418	6	.000335
7	.000080	7	.0525	7	.8225	7	.6694	7	.0391	7	.000313
8	.000090	8	.0549	8	.8363	8	.6565	8	.0366	8	.000291
9	.000104	9	.0574	9	.8495	9	.6437	9	.0343	9	.000270
390	**.00012**	**460**	**.060**	**530**	**.862**	**600**	**.631**	**670**	**.032**	**740**	**.00025**
1	.000138	1	.0627	1	.8739	1	.6182	1	.0299	1	.000231
2	.000155	2	.0654	2	.8851	2	.6054	2	.0280	2	.000214
3	.000173	3	.0681	3	.8956	3	.5926	3	.0263	3	.000198
4	.000193	4	.0709	4	.9056	4	.5797	4	.0247	4	.000185
5	.000215	5	.0739	5	.9149	5	.5668	5	.0232	5	.000172
6	.000241	6	.0769	6	.9238	6	.5539	6	.0219	6	.000160
7	.000272	7	.0802	7	.9320	7	.5410	7	.0206	7	.000149
8	.000308	8	.0836	8	.9398	8	.5282	8	.0194	8	.000139
9	.000350	9	.0872	9	.9471	9	.5156	9	.0182	9	.000130
400	**.0004**	**470**	**.091**	**540**	**.954**	**610**	**.503**	**680**	**.017**	**750**	**.00012**
1	.00045	1	.0950	1	.9604	1	.4905	1	.01585	1	.000111
2	.00049	2	.0992	2	.9661	2	.4781	2	.01477	2	.000103
3	.00054	3	.1035	3	.9713	3	.4658	3	.01376	3	.000096
4	.00059	4	.1080	4	.9760	4	.4535	4	.01281	4	.000090
5	.00064	5	.1126	5	.9803	5	.4412	5	.01192	5	.000084
6	.00071	6	.1175	6	.9840	6	.4291	6	.01108	6	.000078
7	.00080	7	.1225	7	.9873	7	.4170	7	.01030	7	.000074
8	.00090	8	.1278	8	.9902	8	.4049	8	.00956	8	.000069
9	.00104	9	.1333	9	.9928	9	.3929	9	.00886	9	.000064
410	**.0012**	**480**	**.139**	**550**	**.995**	**620**	**.381**	**690**	**.0082**	**760**	**.00006**
1	.00138	1	.1448	1	.9969	1	.3690	1	.00759	1	.000056
2	.00156	2	.1507	2	.9983	2	.3570	2	.00705	2	.000052
3	.00174	3	.1567	3	.9994	3	.3449	3	.00656	3	.000048
4	.00195	4	.1629	4	1.0000	4	.3329	4	.00612	4	.000045
5	.00218	5	.1693	5	1.0002	5	.3210	5	.00572	5	.000042
6	.00244	6	.1761	6	1.0001	6	.3092	6	.00536	6	.000039
7	.00274	7	.1833	7	.9995	7	.2977	7	.00503	7	.000037
8	.00310	8	.1909	8	.9984	8	.2864	8	.00471	8	.000035
9	.00352	9	.1991	9	.9969	9	.2755	9	.00440	9	.000032
420	**.0040**	**490**	**.208**	**560**	**.995**	**630**	**.265**	**700**	**.0041**	**770**	**.00003**
1	.00455	1	.2173	1	.9926	1	.2548	1	.00381		
2	.00515	2	.2270	2	.9898	2	.2450	2	.00355		
3	.00581	3	.2371	3	.9865	3	.2354	3	.00332		
4	.00651	4	.2476	4	.9828	4	.2261	4	.00310		
5	.00726	5	.2586	5	.9786	5	.2170	5	.00291		
6	.00806	6	.2701	6	.9741	6	.2082	6	.00273		
7	.00889	7	.2823	7	.9691	7	.1996	7	.00256		
8	.00976	8	.2951	8	.9638	8	.1912	8	.00241		
9	.01066	9	.3087	9	.9581	9	.1830	9	.00225		
430	**.0116**	**500**	**.323**	**570**	**.952**	**640**	**.175**	**710**	**.0021**		
1	.01257	1	.3382	1	.9455	1	.1672	1	.001954		
2	.01358	2	.3544	2	.9386	2	.1596	2	.001821		
3	.01463	3	.3714	3	.9312	3	.1523	3	.001699		
4	.01571	4	.3890	4	.9235	4	.1452	4	.001587		
5	.01684	5	.4073	5	.9154	5	.1382	5	.001483		
6	.01800	6	.4259	6	.9069	6	.1316	6	.001387		
7	.01920	7	.4450	7	.8981	7	.1251	7	.001297		
8	.02043	8	.4642	8	.8890	8	.1188	8	.001212		
9	.02170	9	.4836	9	.8796	9	.1128	9	.001130		
440	**.023**	**510**	**.503**	**580**	**0.870**	**650**	**.107**	**720**	**.00105**		
1	.0243	1	.5229	1	.8600	1	.1014	1	.000975		
2	.0257	2	.5436	2	.8496	2	.0961	2	.000907		
3	.0270	3	.5648	3	.8388	3	.0910	3	.000845		
4	.0284	4	.5865	4	.8277	4	.0862	4	.000788		
5	.0298	5	.6082	5	.8163	5	.0816	5	.000736		
6	.0313	6	.6299	6	.8046	6	.0771	6	.000688		
7	.0329	7	.6511	7	.7928	7	.0729	7	.000644		
8	.0345	8	.6717	8	.7809	8	.0688	8	.000601		
9	.0362	9	.6914	9	.7690	9	.0648	9	.000560		

The values of Table 5 result from carrying the computation out to at least one more significant figure than has been reported; they differ from the values which would result from the rigorous application of the formula, therefore, by an amount in every case less than 1 in the last figure reported.

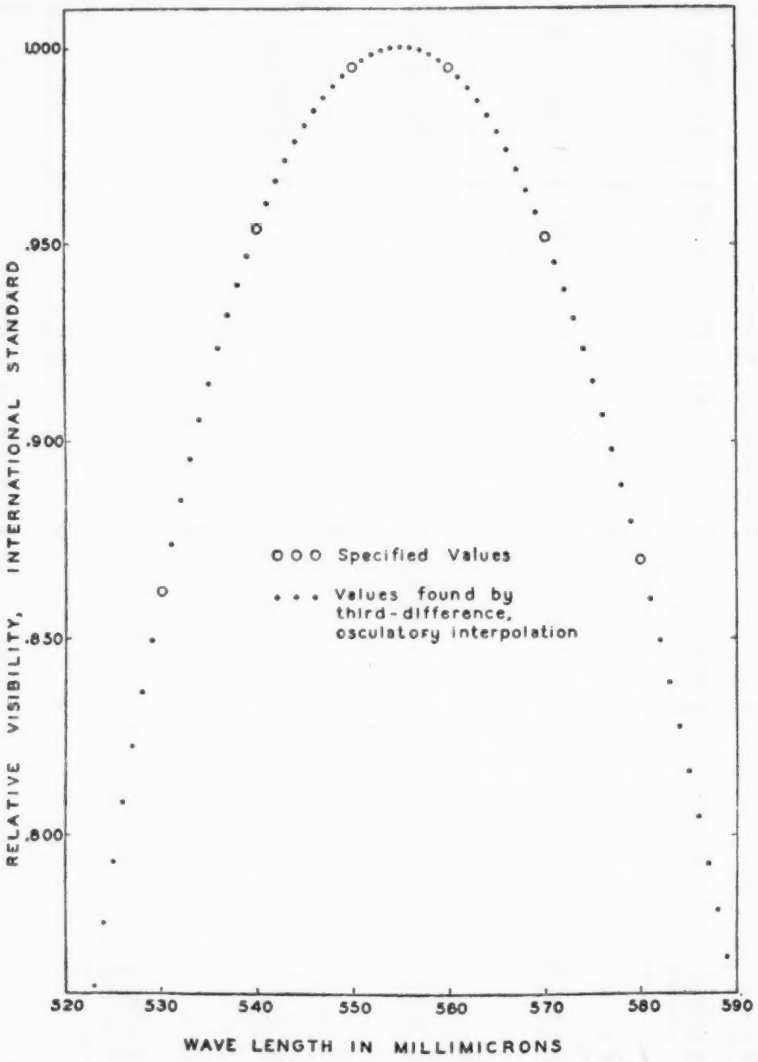

FIGURE 1.—*An example of interpolation of the standard visibility function by the third-difference, osculatory formula*

A portion of the visibility curve near its maximum is chosen for a demonstration of the smoothness of the interpolated values

It is, perhaps, of interest to note that the maximum value of the visibility function according to third-difference osculatory interpolation (see Table 4, Table 5, or fig. 1) is nearly unity, and hence agrees to within 3 in the fourth decimal with the value given by

Gibson and Tyndall from graphical interpolation; and, to be sure, the wave length of the maximum visibility is also very closely 555 mμ as they found.

Figure 1 serves to indicate graphically for a restricted wave-length range the regularity of the interpolated values which are shown as small circles. The values originally specified at every 10 mμ are plotted as large circles.

Acknowledgment is due Miss Mabel E. Brown for carrying out the computations.

WASHINGTON, December, 1930.

DURABILITY AND STRENGTH OF BOND BETWEEN MORTAR AND BRICK

By L. A. Palmer[1] and J. V. Hall[1]

ABSTRACT

Durability and strength of bond between the mortar and brick of 1,296 brick-mortar units have been studied. The materials used included five different makes of brick and two different mortars. Alternate freezing and thawing of moisture-saturated units 50 times followed by drying constituted the tests for bond durability. Strength of bond was determined after storage of other units for six months under three different conditions. Bond durability was increased 100 per cent by loading the units during weathering tests. The factors—pressure on the mortar joint, type of mortar used, degree of wetting the brick, and apparent shrinkage of mortar—were of more importance relatively in their effect upon bond strength or durability than properties of the brick themselves.

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I. INTRODUCTION

1. PURPOSE OF THE INVESTIGATION

The marked degree of adhesion of mortar to brick is often noticed when old brick buildings are torn down. However, as was indicated in a previous publication, "Wet Walls and Efflorescence,"[2] where masonry is very freely exposed to adverse climatic conditions, cracks between mortar and masonry units are sometimes developed. That there are certain precautions which must be observed in matters relating to the design, construction, and maintenance of a building is a fact that was emphasized in that publication. The work herein outlined has been a continuation of this study.

That the mortar joints between masonry units may become disengaged from the units in undrained, horizontal exposures has been recognized. It is essential that the mechanism of the destruction of adhesion of mortar to brick, as well as to other masonry units, be better understood. That such failure is by no means confined to brickwork may be verified by field study. This fact is also illustrated by photographs in the publication mentioned above.

It is believed that too much stress has been placed, in the past, on the inherent strength of masonry materials while other properties may be of equal or even greater importance. It is conceivable that if the mortar and the unit undergo differential volume changes, then the two materials, unit and mortar, may become separated. This condition may lead to excessive water penetration. The purpose of this research was to find answers to such questions as the following:

Is "durability" of "bond" necessarily related to the "strength" of "bond" that may be developed?

All other things being constant, does either the "durability" or the "strength" of bond depend upon the type of brick used and if so, to what extent?

Does shrinkage of mortar tend to decrease the life of the "bond"?

Is the "bond" in a mortar joint that for the most part is not load-bearing, as "durable" as that in a load-bearing one?

Of two classes of masonry mortars that are being widely used, one a mixture of 1 volume of Portland cement to 3 volumes of sand, and the other a mixture of 1 volume of hydrated lime to 1 volume of Portland cement to 6 volumes of sand, would two such mortars exhibit a difference in "durability" of "bond"?

What effect has the degree of wetting brick (when laying them) upon either the "durability" or the "strength" of "bond"?

Is it good practice to always wet all brick when laying them in a wall?

Answers to these questions should point the way to improving the bond between mortar and brick. The field work[3] had already indicated that the most vulnerable points in brickwork are between the brick and the mortar, and that generally the materials themselves are as weather resistant as may be desired.

2. DEFINITION OF TERMS

Bond.—The term "bond" as used herein, denotes a condition; that is, adhesion of mortar to brick.

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[2] Wet Walls and Efflorescence, publication of the American Face Brick Association, A. I. A. file No. 5m.

[3] See footnote 2, p.

Durability.—The length of time that a mortar adheres to a brick is a measure of the "bond durability."

Strength.—"Strength of bond" is the degree of adherence of mortar to brick, expressed in terms of units of stress, such as pounds per square inch of bonded area.

Unit.—The term "unit" as used throughout this paper has reference to two bricks bonded together with mortar. A "loaded" unit is one to which a pressure, perpendicular to the plane of the mortar bed, is maintained throughout the tests for durability of bond.

Wetted.—The term "wetted" refers to a test procedure and is defined under Section II, 3.

3. MATERIALS

The lime used in the mortar conformed to the requirements of Federal Specifications Board specification No. 249 for masons' hydrated lime. The Portland cement met the requirements of Federal Specification for Portland cement as contained in Bureau of Standards Circular 33, fourth edition. Fairly clean Potomac River sand that had passed a No. 8 sieve was used. The screen analysis of this sand was as follows:

	Per cent
Through No. 8, retained on No. 20	9. 17
Through No. 20, retained on No. 30	23. 00
Through No. 30, retained on No. 50	59. 20
Through No. 50, retained on No. 100	7. 70
Through No. 100	. 88
Total	99. 95

Only marketable brick, made both from clay and from shale, were selected. A description of the five different manufacturers' brick used is as follows:

Brick No. 1.—Made from surface clay, molded dry-press; absorption range, 9.5 to 15.5 per cent; very high rate of absorption; specimens "wetted" from end to end within 30 minutes.

Brick No. 2.—Same as No. 1 except that absorption range was between the limits 11.5 to 17.0 per cent; very high rate of absorption; specimens tested "wetted" from end to end within one hour.

Brick No. 3.—Side-cut, stiff-mud brick, made from fire clay; absorption 4.8 to 9.8 per cent; very low rate of absorption; from four to six hours were required to "wet" specimens of this make from edge to edge.

Brick No. 4.—Side-cut, stiff-mud shale; absorption 5.2 to 10.7 per cent; very low rate of absorption; from 8 to 12 hours were required to "wet" through edge to edge, specimens of this make of brick.

Brick No. 5.—Side-cut, stiff-mud shale; absorption 6.0 to 11.5 per cent; very low rate of absorption; from four to six hours were required to "wet" specimens of this make of brick from edge to edge.

II. METHODS OF TEST

1. TOTAL ABSORPTION

Total absorption was determined by immersing brick for a period of 48 hours in water at normal room temperature, the dry weight having been previously determined by drying at 150° C. to constant weight. The water absorbed was computed as percentage of the initial dry weight of the specimen.

2. CLASSIFICATION OF BRICK SHIPMENTS

Each manufacturer's shipment of brick was divided into six groups. Each of these six groups represented a certain limited range in absorption. For example, the range of absorption for the six groups of brick No. 1 were: Group 1, 9.5 to 10.5 per cent, inclusive; Group 2, 10.6 to 11.5 per cent, inclusive; Group 3, 11.6 to 12.5 per cent inclusive; Group 4, 12.6 to 13.5 per cent, inclusive; Group 5, 13.6 to 14.5 per cent, inclusive; and, Group 6, 14.6 to 15.5 per cent, inclusive. Two brick of the same group (never from different groups) were bonded together with mortar.

3. RATE OF ABSORPTION

The rate of absorption was determined in the following manner. Brick were stood either on end or on edge in about 1 inch of water and the time taken for water to rise by capillarity to the upper surface was observed and recorded. The number so tested was 60 for each manufacturer's shipment. When the rate of absorption was such that more than one hour was required to wet the specimens from end to end, these tests were conducted in a humid chamber to prevent excessive evaporation from the surfaces.

4. PREPARATION OF SPECIMENS

Bricks were set under three conditions, namely, dry, 50 per cent saturated and 80 per cent saturated. The gain in weight equivalent to the desired degree of saturation was computed from the known amount of total water absorption as previously determined. The specimens were immersed in water, and removed and weighed periodically, until the predetermined gain in weight was reached.

5. MORTARS USED

Two mortars were used One of these was the rather widely used 1:1:6 mortar, the numbers referring to proportions by volume of lime, Portland cement and sand, respectively. The other contained only Portland cement and sand in the ratio, 1:3 by volume. The amount of mixing water was 16.2 per cent of the total weight of water, lime, cement, and sand in the 1:1:6 mix and 15.2 per cent of the weight of water, cement, and sand in the 1:3 mortar. The five types of brick were used with one mortar (1:1:6) in the study of bond durability and strength as related to different makes of brick. One type of brick (No. 5) was used in the study of strength and durability of bond obtained with two different mortars; that is, the mixes, 1:1:6 and 1:3.

6. PREPARATION OF UNITS FOR TEST

The mortar joints at the time of forming the units were three-eighths inch in thickness. Brass lugs, three-eighths inch in height, were embedded in the mortar joint of one-half of all of the units. Each lug was covered by a thin layer of mortar so that metal and brick would not be in intimate contact and a more even bearing surface could be secured. Three lugs were embedded in a joint, two near one end of the horizontal joint (all brick being laid together flatwise) and about 2½ inches apart and a third at the other end and opposite the mid point on a line joining the first two lugs. In units made without lugs it was

somewhat more difficult to obtain joints of uniform thickness. However, with care and practice, the variation in thickness of joints even in these cases was kept within reasonable limits.

In order that the mortar might not be allowed to remain too long before use, one batch sufficient in quantity to bond together six units was made at a time. Joints were made flush and immediately upon placing the upper brick on the layer of mortar on the brick beneath, the operator's full weight was applied to the top brick for about one minute so as to produce intimate contact between mortar and brick.

This latter procedure was modified when it was desired to study the effect of maintaining a pressure perpendicular to the bed of mortar throughout the whole period of testing. In this case a band of drilled strap iron (holes at half-inch intervals) was fitted about the middle of the unit and a machine bolt, ¼ by 2 inches (20 threads per inch), was placed through the overlapping holes. The threaded end rested in a depression in an iron plate lying at the center of the upper surface of the top brick, a nut on the bolt being beneath the overlapping bands. The unit was thus strapped at the time of forming it and an indefinite load was applied by turning the bolt with a 6-inch lever. Forty-eight hours after forming the unit, the band was made as tight as possible by applying a force of about 150 pounds at the end of the 6-inch lever arm. When the same procedure was followed, using a proving ring instead of a unit, it was found that the total pressure obtained varied from 500 to 800 pounds. Due to some degree of plastic flow and to shrinkages and expansions in the mortar during the process of testing, this load could not, of course, remain constant. It was observed that the bolts generally remained very tight, this condition being checked at the end of a definite period of storage of the units and prior to freezing and thawing tests. Although the load on these units was not constant, it was considered that it was at least as great at all times as that on masonry units in walls typical of modern methods of construction.

7. TEST PROCEDURE

(a) STORAGE OF UNITS

All units remained in the laboratory during the first 48 hours. The temperature range in the laboratory was from 15° to 32° C., the average being about 20° C. The relative humidity varied from 20 to 80 per cent, but usually was within the limits, 30 to 50 per cent.

The procedure followed with bricks Nos. 1 to 4, inclusive, using the 1:1:6 mortar only, and brick No. 5 using both the 1:3 and the 1:1:6 mortars, is given in Table 1. The six units in the smallest subdivision of units (Table 1) represented the six groups of each shipment as based on percentage absorption. Thus each group of each shipment of brick was represented in every one of the final subdivisions of six units. After remaining for 48 hours in the laboratory, equal numbers of the units were stored under the following conditions: In the laboratory, out of doors, and in a room wherein the relative humidity was fairly constant (approximately 95 per cent) and the temperature was 70° F. Units which underwent durability tests remained in storage for two months prior to such tests. Units which did not undergo durability tests remained in storage for six months, at the end of which time the strength of bond was determined.

TABLE 1.—*Outline of procedure*

Bricks 1, 2, 3, and 4. Total number of units for one make of brick and one mortar, 216.	With lugs, 108 units	Stored outdoors, 36 units	Brick set dry, 12 units.[1]
			Brick 50 per cent saturated, 12 units.[1]
			Brick 80 per cent saturated, 12 units.[1]
		Stored in laboratory, 36 units	Brick set dry, 12 units.[1]
			Brick 50 per cent saturated, 12 units.[1]
			Brick 80 per cent saturated, 12 units.[1]
		Stored in humid room, 36 units	Brick set dry, 12 units.[1]
			Brick 50 per cent saturated, 12 units.[1]
			Brick 80 per cent saturated, 12 units.[1]
	Without lugs, 108 units	Stored outdoors, 36 units	Brick set dry, 12 units.[1]
			Brick 50 per cent saturated, 12 units.[1]
			Brick 80 per cent saturated, 12 units.[1]
		Stored in laboratory, 36 units	Brick set dry, 12 units.[1]
			Brick 50 per cent saturated, 12 units.[1]
			Brick 80 per cent saturated, 12 units.[1]
		Stored in humid room, 36 units	Brick set dry, 12 units.[1]
			Brick 50 per cent saturated, 12 units.[1]
			Brick 80 per cent saturated, 12 units.[1]
Brick No. 5. Total number of units, 432.	The procedures followed were the same as those for bricks 1 to 4, inclusive, with the following exceptions: Two different mortars (1:1:6 and 1:3) were used, 216 units being made with each mortar; all of the units were tested for bond durability. Among each of the two lots of 216 units, one-half were and one-half were not loaded.		

[1] 6 units tested for durability and an equal number for strength of bond.

(b) TESTS FOR BOND DURABILITY

After storage for two months those units undergoing durability tests were removed, immersed for 48 hours in water, then placed in pans containing a half-inch of water (flat side of bottom brick of unit down) and conveyed to a freezing chamber where they remained for about 18 hours. They were then thawed by immersion in water maintained at about normal room temperature. One freezing followed by one thawing constituted a cycle. There were 50 such cycles. Following each thawing, the units were examined and any bond failures were noted. It was considered that the bond had failed, when on picking up the unit by the top brick, the lower one became separated from it.

Following the 50 cycles of freezing and thawing, the "survivors" among all units so tested were dried for three weeks on the upper shelf of a large gas oven at a temperature ranging from 80° to 100° F. During this drying procedure the bond failed in many instances. It was, of course, impossible to assign any definite share of such failure to the drying operation alone, the bond having been most likely weakened previously in the weathering tests. In every instance, units which survived the bond durability tests were reserved for tests for strength of bond.

(c) STRENGTH OF BOND

The half of all of the units made and which remained in storage for a period of six months were removed after this period of time and, together with those units which survived the durability tests, were dried for three weeks. After drying, the units were coated with plaster of Paris, the plaster being applied over the edges of the brick and mortar. The unit lying on its side was pressed down into a sufficient quantity of plaster of Paris paste of proper consistency spread on a glass plate. A similar quantity of the paste was then applied on the upper surface of the unit as it rested in the lower plaster bed. By means of accurately machined spacers between the bottom glass plate and an upper one pressed down on the top bed of plaster, parallelism of the two opposite plastered surfaces was assured. The excess plaster was trimmed away from the edges and, after setting, the plates could be easily removed without cracking the plaster. The thickness of the plaster coat on the two opposite longitudinal faces of the unit was about one-sixteenth to one-eighth inch. After hardening, the plaster covering the mortar joint was carefully removed by means of a hacksaw and a steel spatula.

The device for gripping the unit in testing for strength of bond was a slight modification of that described by McBurney [4] in his study of the strength of brick in tension. This device is illustrated by Figures 1 and 2. Steel shims of different degrees of thickness could be inserted between the wedges, *W*, and the steel faces, *F*, and allowed for variations in thicknesses of the plastered brick. The downward pull on the lower block gripping the lower brick was applied slowly. With the machine in low gear this downward movement of the head was 0.01 of an inch per minute. Actually, the travel of the block was less, due to the slow taking up of slack in the

[4] J. W. McBurney, Strength of Bond in Tension, J. Am. Ceramic Soc., 2, No. 2; February, 1928.

gripping device. S and S' (fig. 2) represent concentric steel surfaces separated by ¼-inch steel balls. The radius of curvature of the outer spherical surface was 6.9 inches in each case, bringing the center of curvature within the center of the mortar joint, M. To keep the lower block from falling back on the head of the machine when the units were pulled apart, heavy metal "safety straps" were bent and suspended from the upper block so as to catch the lower one when it fell.

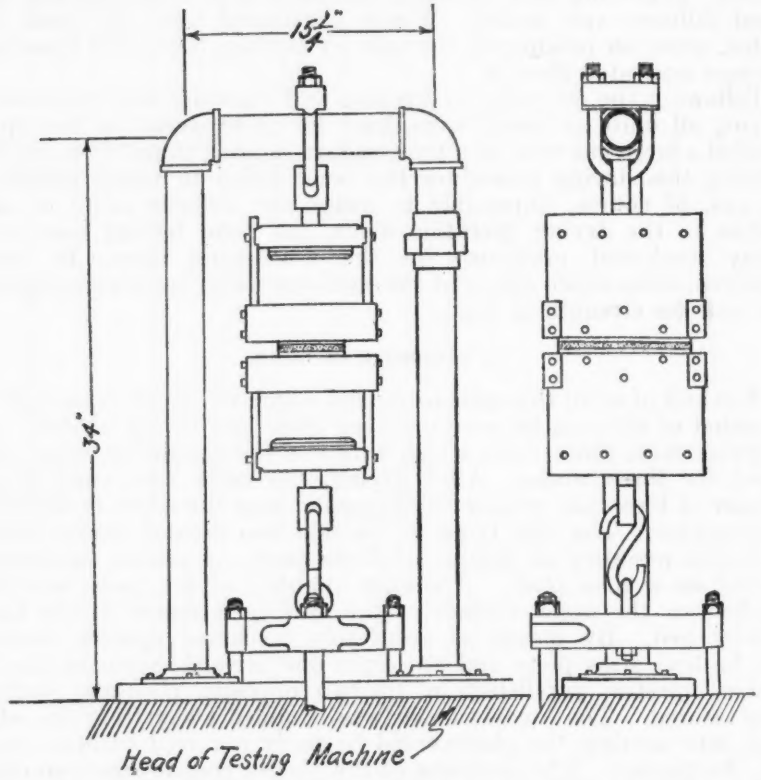

FIGURE 1.—*Assembled apparatus used in testing units in tension*

In computing the data relative to tests for strength of bond the total load was divided by the total area of the mortar bed, the dimensions of the latter being measured by a rule marked in tenths of an inch. Unbonded areas were not deducted in any case from the total area.

III. RESULTS

Brick Nos. 1 and 2 absorbed water far more rapidly than Nos. 3, 4, and 5, and it soon became evident that failure to have specimens of the former at least 80 per cent saturated at the time of laying them, constituted poor workmanship. However, this type of poor workmanship was one of the variable factors to be studied. Specimens of brick Nos. 1 and 2 when not wetted sufficiently, dried the wet

mortar very quickly when it was applied, thereby making it difficult to obtain a good mechanical bond initially. This apparently was not the case with brick Nos. 3, 4, and 5. It will be shown later (Pt. III, sec. 2) that failure to have specimens of brick Nos. 1 and 2 sufficiently saturated when laying them resulted in "patches" of unbonded areas. Apparently, wetting specimens of brick Nos. 3, 4, and 5 did not interfere with the development of a good mechanical bond, but would seem to be an unnecessary operation and might detract from the neatness of construction.

For these reasons, only those results for durability and strength tests obtained with the units made from brick Nos. 1 and 2 in which

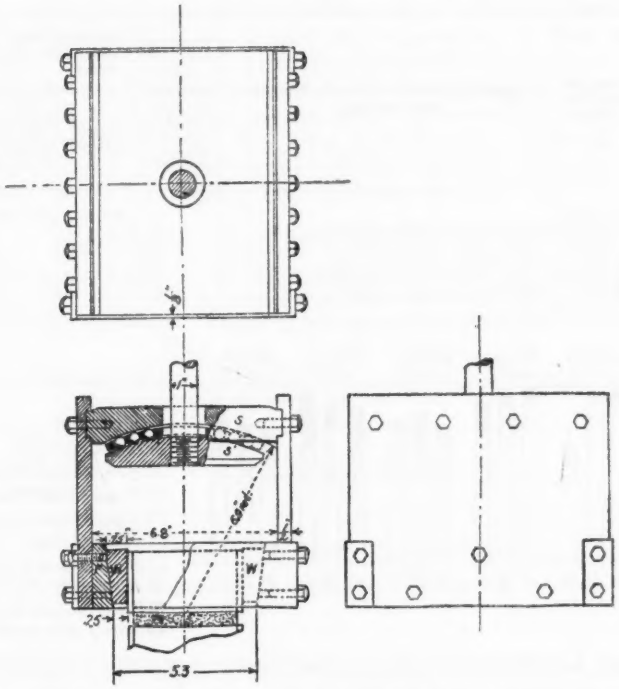

FIGURE 2.—*Details of spherical bearing and grips for apparatus*

the specimens were 80 per cent saturated when set, are considered in the averages, except in those instances wherein the degree of saturation of the brick is the particular variable considered.

1. DURABILITY OF BOND

It must be realized that this test was very severe. For comparative data the results should be indicative of the importance of various factors involved in the durability of bond. It must not be considered that the large number of failures of bond is indicative of any glaring defect in brickwork. It is not possible to duplicate in every respect, in laboratory tests, conditions obtaining in a wall and to complete such tests during any reasonable length of time. Con-

sequently the results may often be misleading if this fact is not appreciated and thoroughly borne in mind.

The average percentage failures of bond during the tests are given in the following tabulations of results.

(a) DURABILITY OF BOND AS AFFECTED BY THE DEGREE OF WETTING DIFFERENT BRICK

Consider first the durability of bond as affected by the degree of wetting the different brick at the time of forming the units. This is illustrated by the data in Table 2.

TABLE 2.—*Effect of wetting brick*

Brick	Total absorption (range)	Rate of absorption (time in hours to wet through)	Number of test units averaged for each condition of wetting	Failure of bond (1 : 1 : 6 mortar, units with and without lugs)		
				Brick set dry	Brick 50 per cent saturated when set	Brick 80 per cent saturated when set
	Per cent			*Per cent*	*Per cent*	*Per cent*
No. 1	9. 5–15. 5	¼ to ½ hour (end to end)	36	97	97	67
No. 2	11. 5–17. 5	¾ to 1 hour (end to end)	36	100	94	92
No. 3	4. 8–9. 8	4 to 6 hours (edge to edge)	36	78	86	81
No. 4	5. 2–10. 7	6 to 12 hours (edge to edge)	36	89	89	97
No. 5	6. 0–11. 5	4 to 6 hours (edge to edge)	36	75	77	83

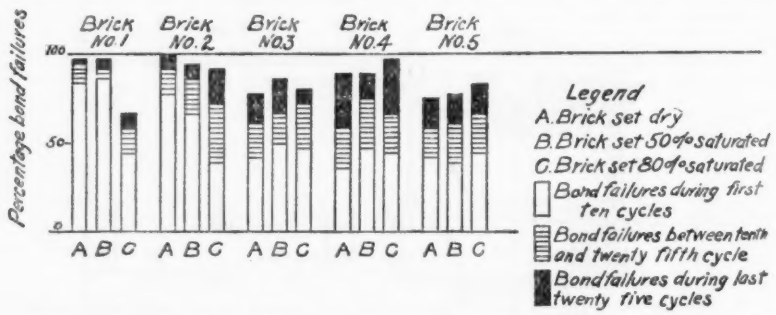

FIGURE 3.—*Bond durability as related to degree of wetting different brick*

Figure 3 shows the approximate rates of bond failures (given in Table 2) during the first 10, between the tenth and twenty-fifth, and between the twenty-fifth and fiftieth freezing and thawing cycles. It is evident that wetting specimens of bricks Nos. 1 and 2 tended to markedly reduce the percentage failures of bond during the first 10 cycles. However, from Figure 3 it is apparent that this was not so in the case of units made with brick Nos. 3, 4, and 5. It is seen that the distributions of percentage bond failures for units with these brick over the intervals considered are much more uniform for the three conditions of wetting than obtains in the case of brick Nos. 1 and 2. It is noted, however, that the greatest number of bond failures per cycle occurred during the first 10 cycles in all cases.

From Table 2 it is clearly evident that marked improvement in bond durability in units made with brick No. 1 was effected by having specimens of this brick 80 per cent saturated when set. It is not so

evident from Table 2 that this was so in the case of brick No. 2. As noted above, however, the number of bond failures during the first 10 cycles was markedly decreased by having specimens of this brick 80 per cent saturated. It might be also concluded that neither harm nor good resulted from wetting specimens of brick Nos. 3 and 5. The data indicate that there was some slight improvement in bond durability with units containing brick No. 4 by having specimens of this brick completely dry when forming the units.

The effect of wetting or not wetting specimens of brick Nos. 1 and 2 is further illustrated by the data of Table 12 where strength of bond is considered.

Specimens of brick No. 2 contained from 12 to 15 per cent lime, particles of such being clearly visible. It is believed that hydration of this uncombined lime caused an expansion of the specimens. Brick Nos. 1 and 2 had very similar properties aside from their free lime contents (specimens of brick No. 1 containing no lime particles) and it is likely that the percentage bond failures with brick No. 2 was higher than that for brick No. 1 for this reason. Some of the specimens of brick No. 2 when tested individually (not in units) began to disintegrate after 80 freezing and thawing cycles.

(b) BOND DURABILITY AS RELATED TO BRICK USED

The data of Table 2 are rearranged to indicate the variation in durability of bond which may be expected when dissimilar brick are used with one mortar. These data appear in Table 3.

TABLE 3.—*Variation of bond durability with respect to brick used (1 : 1 : 6 mortar, units with and without lugs)*

Brick	Number of units averaged	Percentage failures during tests	
No. 1	36	67	Average for smooth, porous dry-press brick, 80 per cent.
No. 2	36	92	
No. 3	108	82	Average for rough, relatively impervious brick, 84 per cent.
No. 4	108	92	
No. 5	108	79	

There have been numerous opinions expressed to the effect that a relatively dense and impervious brick will not bond with mortar. The data of Table 3 indicate that such is not the case, but that brick may vary quite widely in absorption properties without affecting materially the life of the bond. In fact the average of failures for brick No. 4, representative of the densest material, is no greater than that of No. 2, the most porous material considdered here.

(c) EFFECT OF METAL LUGS IN MORTAR

It is interesting to note the effect of the presence of the lugs embedded in the mortar on the durability of bond. This is shown by the data in Table 4.

TABLE 4.—*Effect of lugs on bond durability (1 : 1 : 6 mortar)*

Brick	Number of units averaged		Failures during tests	
	Units with lugs	Units without lugs	Units with lugs	Units without lugs
			Per cent	*Per cent*
No. 1	18	18	100	33
No. 2	18	18	100	83
No. 3	54	54	94	69
No. 4	54	54	94	91
No. 5	54	54	88	69
Average			95	69

With five different types of brick bonded together with one (1 : 1: 6) mortar, the units in each of the five cases having been stored under identical conditions and all other conditions of test being the same, the durability of bond was less, without a single exception, when lugs were embedded in the joint. This indicates that shrinkage of mortar during the period of storage may have weakened the bond between the brick and mortar because the brick were not free to move toward one another and may have been torn loose in places from the cementing material. The grand average for the five different makes of brick under the conditions of testing is 95 per cent failures with, and 69 per cent failures without, lugs. This may in part explain the observation that cracks are more apt to occur in vertical than in horizontal joints, since it is obvious that brick are usually not free to move horizontally toward each other.

(d) DURABILITY OF BOND AS RELATED TO ABSORPTION

As stated above, each manufacturer's brick shipment was divided into six groups, each group containing specimens of very nearly the same absorption. Any relation existing between absorption and bond durability is further emphasized by considering the group averages within each shipment of brick. The resulting averages are given in Table 5.

TABLE 5.—*Durability of bond versus degree of absorption of brick (1 : 1 : 6 mortar, with and without lugs)*

Brick	Units formed with brick of groups 1 to 3, inclusive, lower range of absorption			Units formed with brick of groups 4 to 6, inclusive, higher range of absorption		
	Absorption range	Bond failures	Number averaged	Absorption range	Bond failures	Number averaged
	Per cent	*Per cent*		*Per cent*	*Per cent*	
No. 1	9. 5–12. 5	68	18	12. 5–15. 5	68	18
No. 2	11. 5–14. 5	94	18	14. 5–17. 5	90	18
No. 3	4. 8– 7. 0	89	54	7. 0– 9. 8	74	54
No. 4	5. 2– 8. 0	94	54	8. 0–10. 7	91	54
No. 5	6. 0– 9. 0	86	54	9. 0–11. 5	71	54
Average		86			79	

The differences in this instance are not significant. With the possible exception of units made with brick Nos. 3 and 5, it is apparent that the durability of bond is not materially affected by variations in the degree of absorption within the limits characteristic of a single shipment.

(e) EFFECT OF STORAGE CONDITIONS

During the two months period of storage prior to freezing and thawing tests it was apparent (Pt. III, sec. 2) that the mortar in units stored out of doors or in the humid room developed a greater strength than that attained in mortar within units stored for the same length of time in dry storage, that is, in the laboratory. It would seem, therefore, that if durability were dependent upon strength, there would be a relatively greater percentage of bond failures among units which had remained in dry storage. In Table 6 the effect of storage on bond durability may be noted.

TABLE 6.—*Effect of storage on bond failure during subsequent durability tests (1 : 1 : 6 mortar, with and without lugs)*

Brick	Number averaged			Failures		
	Outdoor storage	Laboratory storage	Humid room storage	Outdoor storage	Laboratory storage	Humid room storage
				Per cent	*Per cent*	*Per cent*
No. 1	12	12	12	69	50	83
No. 2	12	12	12	92	83	100
No. 3	36	36	36	86	92	67
No. 4	36	36	36	83	100	95
No. 5	72	72	72	73	75	88
Average				81	80	87

Certainly the bond in those units in which the mortar had developed relatively greater strength (Table 9, Pt. III, sec. 2) was no more durable than it was in units wherein the mortar had not become so strong. A consideration of the combined data of the two tables (Nos. 6 and 9) justifies the belief that strength was of no great importance in so far as the durability of the bond in the units was concerned.

(f) DURABILITY OF BOND AS RELATED TO MORTAR

One make of brick, No. 5, was used in the study of comparative durability of bond with two different mortars. The results are given in Table 7.

TABLE 7.—*Durability of bond as related to mortar used (units loaded and not loaded, with and without lugs)*

	Failures during tests	Number averaged
	Per cent	
1:3 Portland cement-sand mortar	48	216
1:1:6 mortar	61	216

It may be mentioned in this connection that in preliminary work by the authors, the dregee of expansion on wetting, and contraction on drying, of this 1:1:6 mortar was found to be somewhat greater than similar volume changes of this 1:3 mortar. This has also been observed by Davis.[5] These changes occurred subsequent to hardening, and under conditions identical in the two cases. It is hoped that much more information relative to volume changes in mortar may be available for a future publication, and too much importance should not be attached to these data of Table 7 at the present time. It may be mentioned that since these tests were made, 1:1:6 mortar mixtures have been found which exhibit volume changes less in magnitude than those characteristic of the straight cement mortar.

(g) EFFECT OF VERTICAL LOADING

One manufacturer's brick (No. 5) was used to study the effect of loading. Comparative durability values are given in Table 8, and include averages for units loaded and not loaded during testing. This includes equal numbers of units made with 1:3 and 1:1:6 mortar.

TABLE 8.—*Durability of bond as increased by a vertical load on bonded units (with 1:1:6 and 1:3 mortar, with and without lugs)*

	Failures of bond during tests	Number averaged
	Per cent	
Units not loaded	73	216
Units loaded	36	216

The averages apply to results obtained from testing 216 units not loaded and an equal number loaded, and should, therefore, be representative. The bond durability was doubled by imposing a pressure perpendicular to the mortar bed. There may be various reasons for this. A continuous pressure so applied may tend to restrain to some extent the forces produced by differential volume changes between brick and mortar. Again, it may insure much more intimate contact between the brick and cementing material. This is probably another reason for the occurrence of cracks between brick and mortar in vertical joints which are, for the most part, nonload bearing.

Figure 4 is an illustration of a typical failure of a nonloaded and Figure 5 is similarly one of a loaded unit during the freezing and thawing tests. Note that there was about equal adherence of mortar to each individual brick in the latter case. (Fig. 5.) As illustrated in Figure 4, the top brick of nonloaded units usually had considerably less mortar adhering to them than the lower brick after failure. Figure 6 illustrates a somewhat unusual case in the progressive failure of bond. Here the mortar sheared loose in part both from the upper and from the lower brick.

That the bond failure was not due to disintegration of either the brick or mortar is indicated by the following facts. When the

[5] Raymond E. Davis and G. W. Troxell, Volumetric Changes in Portland Cement Mortars and concretes, Proc. Am. Concrete Inst., **25**, pp. 210–260; 1929.

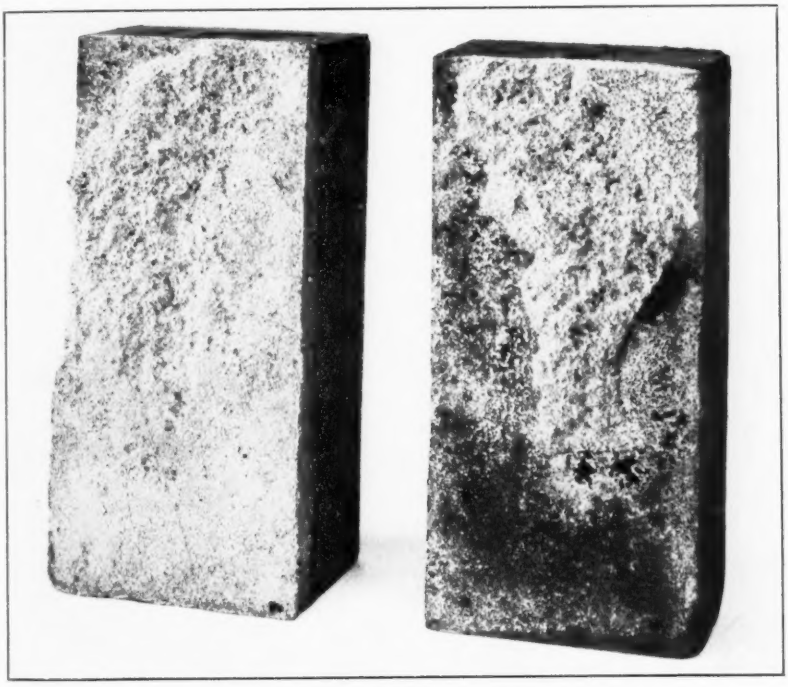

FIGURE 4.—*Typical bond failure in a nonloaded unit*

FIGURE 5.—*Typical bond failure in a loaded unit*

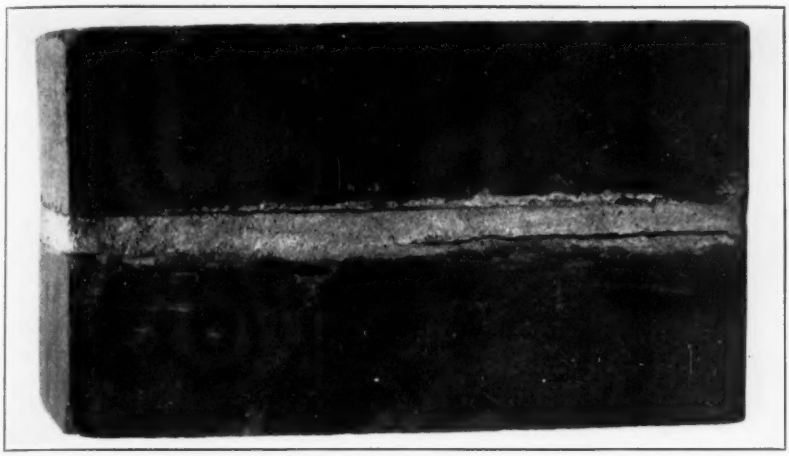

FIGURE 6.—*An unusual case of bond failure*

The mortar, initially well bonded, sheared loose from both brick in the unit during freezing and thawing.

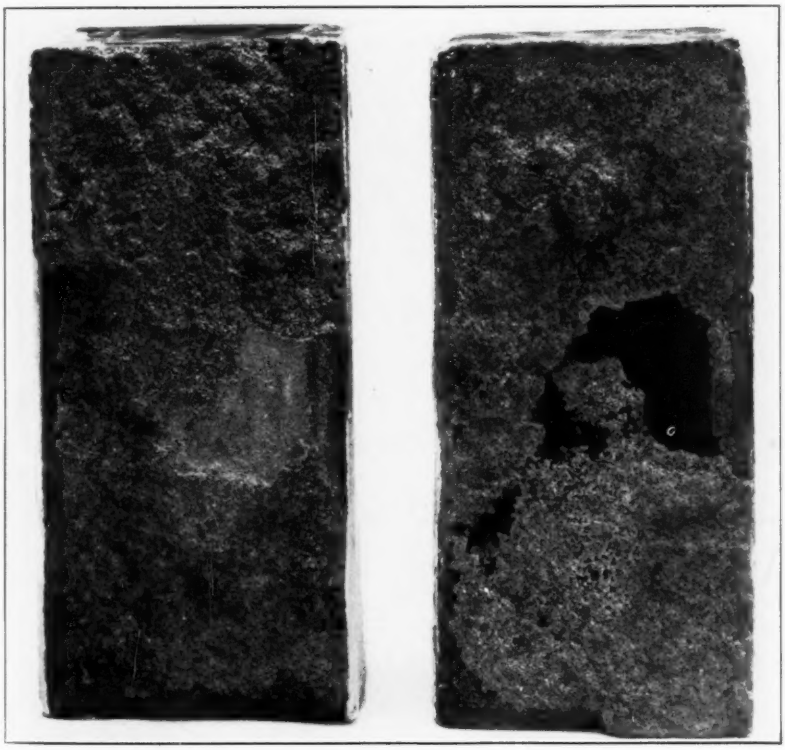

FIGURE 7.—*Effect of not saturating sufficiently a rapidly absorbing brick when laying it in mortar*

Note the unbonded areas.

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strength of bond was determined for units which had survived the freezing and thawing tests, it was found that the degree of adhesion of mortar to brick compared favorably with that obtaining in units formed with the same brick and mortar but which had remained in storage and had not been subjected to freezing and thawing. Moreover, after any failure of bond, the mortar was firm in all cases and not "crumbly." As the photographs (figs. 4, 5, and 6) show, failure apparently was due to stresses between brick and mortar, and it is suggested that this condition may, in part, have been caused by unequal volume changes in the two materials. This will be considered in another report to be published later, and dealing exclusively with volume changes in these materials. It may be stated here, however, that the expansion of these brick on prolonged wetting was relatively small in all cases as compared to the expansion produced by wetting these same mortars used in forming these units.

2. STRENGTH OF BOND

In the study of strength of bond it was proposed to find the relative importance of various factors, such as climatic conditions, the degree of absorption and the roughness of surface of brick, the extent to which a brick is wetted when it is laid up with mortar, and the degree of shrinkage which the mortar may undergo. Each of these is more or less important in determining the development of strength, both in the mortar as a material and in its degree of adhesion to the bonded unit. The units stored outdoors were exposed for the most part to winter conditions. It was impossible to make them all on the same day, but the comparative results as given below refer to units that were taken to their respective storage places within the same two months. This introduced normal variations in conditions of outdoor storage, but the variations in laboratory and humid room storage conditions were relatively small.

(a) STRENGTH OF BOND AS DEPENDENT UPON STORAGE CONDITIONS

In Table 9 are given comparative data showing the effects of storage on strength of bond at the end of six months. The procedure followed in computing the data in Tables 9, 10, and 11 with respect to brick Nos. 1 and 2 was the same as that followed in preparing Tables 3 to 6, inclusive; that is, only data for those units made with brick Nos. 1 and 2 which were 80 per cent saturated were averaged.

TABLE 9.—*Effect of storage conditions (6 months) on strength of bond (1 : 1 : 6 mortar, with and without lugs)*

Brick	Number averaged			Average		
	Outdoor storage	Laboratory storage	Humid room storage	Outdoor storage	Laboratory storage	Humid room storage
				Lbs./in.²	*Lbs./in.²*	*Lbs./in.²*
No. 1	12	12	12	19.3	21.1	25.3
No. 2	12	12	12	51.8	32.7	29.0
No. 3	36	36	36	34.0	16.3	39.4
No. 4	36	36	36	21.6	5.6	28.0
Average				31.7	18.9	30.4

It does not seem that a strong bond is of necessity a durable one. This is brought out by a comparison of the values in Table 9 with those of Table 6 in which durability was considered. The average percentage failures of bond among units stored for two months (Table 6) under these same three conditions, and prior to testing, were (averaging brick 1 to 4, inclusive, only) 81 per cent for outdoor, 80 per cent for laboratory and 86 per cent for humid room storage. It is believed that the stresses induced by freezing and thawing were of such magnitude that the bond failed regardless of strength.

(b) STRENGTH OF BOND AS RELATED TO BRICK

It is usually considered, and it may be true all other things being equal, that a porous brick should be preferred to a more impervious one from the standpoint of bonding with mortar. However, it is reasonable to suppose the degree of roughness of surface to be also a factor of importance. For example, mortar has been known to adhere tenaciously to roughened glass. Brick Nos. 1 and 2 were relatively porous and smooth whereas Nos. 3 and 4 were relatively impervious and rough surfaced. Table 10 gives a direct comparison between these different makes of brick with respect to bonding qualities. These are averages for all conditions of storage and with 1:1:6 mortar. The individual maximum values were obtained with units stored in the humid room and the minimum values with units stored in the laboratory.

TABLE 10.—*Strength of bond with different makes of brick (1 : 1 : 6 mortar, with and without lugs)*

Brick	Average bond strength	Number[a] averaged	Individual maximum	Individual minimum	Percentage of all units exceeding in bond strength 30 Lbs./in.²
	Lbs./in.²		*Lbs./in.²*	*Lbs./in.²*	
No. 1	21.9	36	62.3	0.5	47.2
No. 2	37.8	36	71.5	1.2	72.2
Average	29.9				
No. 3	29.9	108	53.5	.8	28.7
No. 4	18.4	108	63.9	1.3	52.8
Average	24.2				

The averages indicate some improvement in strength of bond through the use of porous brick. However, the difference is not marked. The individual maximum values and the percentages (Table 10) certainly indicate that it is possible to bond satisfactorily a dense, relatively impervious brick. In the case of the individual maxima the tensile strength of the mortar rather than the degree of adhesion of it to brick was measured for, after breaking, practically as much mortar adhered to one brick as adhered to the other. In the case of the minimum values, obtained with units stored in the laboratory, this was not the case. Here the top brick broke "clean" from the mortar.

(c) STRENGTH OF BOND VERSUS ABSORPTION OF BRICK

In considering brick molded by the same process and from the same clay or shale, are the relatively more porous brick bonded more strongly? It may seem that this question has already been considered in Table 10. However, in that case different makes of brick were considered. In Table 11 averages similar to those of Table 5 are given and show no significant difference.

TABLE 11.—*Effect of apparent porosity of brick on strength of bond (1 : 1 : 6 mortar, with and without lugs)*

Brick	Units formed with brick of groups 1 to 3, inclusive, lower range of absorption			Units formed with brick of groups 4 to 6, inclusive, high range of absorption		
	Absorption range	Strength of bond, average	Number averaged	Absorption range	Strength of bond, average	Number averaged
	Per cent	*Lbs./in.²*		*Per cent*	*Lbs./in.²*	
No. 1	9. 5–12. 5	23. 7	18	12. 5–15. 5	20. 9	18
No. 2	11. 5–14. 5	36. 8	18	14. 5–17. 5	38. 8	18
No. 3	4. 8– 7. 0	36. 3	54	7. 0– 9. 8	23. 5	54
No. 4	5. 2– 8. 0	19. 5	54	8. 0–10. 7	17. 0	54
Average		29. 1			25. 0	

(d) STRENGTH OF BOND AS RELATED TO DEGREE OF WETTING BRICK

Although data obtained with units of brick 1 and 2, set dry and 50 per cent saturated, are not included in the averages given in Tables 9, 10, and 11, they have been considered. Averages, including values obtained with all conditions of saturation, are given in Table 12.

TABLE 12.—*Effect of degree of wetting brick on strength of bond. Averages for 36 units (1 : 1 : 6 mortar, with and without lugs)*

Brick	Average		
	Brick 80 per cent saturated	Brick 50 per cent saturated	Brick set dry
	Lbs./in.²	*Lbs./in.²*	*Lbs./in.²*
No. 1	21. 9	9. 6	6. 8
No. 2	37. 8	16. 0	0. 5
No. 3	25. 6	29. 1	35. 0
No. 4	20. 1	17. 1	18. 0

Figure 7 illustrates the effect of not wetting sufficiently a rapidly absorbing brick at the time of laying it in a wall. In this case, the two individual brick of type No. 1 were 50 per cent saturated when the unit was formed. Note the unbonded areas. In this connection one should realize that it is the rate rather than the amount of absorption that must be given most consideration. A rapidly absorbing brick tends to dry the wet mortar very quickly when it is first applied. When so quickly dried, the mortar loses plasticity and does not make intimate contact with the entire surface as it should. At the same time a brick when laid should not be so thoroughly saturated that it can absorb no water. A little suction is necessary to form the best

bond. It is difficult to draw any definite line even for one particular make of brick; however each brick manufacturer should study his material and be able to make recommendations to the user as to the proper degree of wetting his brick.

(e) EFFECT OF METAL LUGS

In Table 13 are given results which may indicate the effect of restraining any movement of the brick in a direction perpendicular to the plane of the mortar bed. As already described, this was accomplished by embedding brass lugs in the mortar. The possible reasons for these differences have already been discussed in connection with the data of Table 4 which tend to corroborate those in Table 13.

TABLE 13.—*Effect of lugs on bond strength (1 : 1 : 6 mortar)*

Brick	Number averaged		Bond strength, average of all units	
	Units with lugs	Units without lugs	Units with lugs	Units without lugs
			Lbs./in.²	*Lbs./in.²*
No. 1	18	18	7.9	35.9
No. 2	18	18	34.1	41.6
No. 3	54	54	9.3	50.5
No. 4	54	54	9.5	27.3
Average			15.2	38.8

(f) STRENGTH OF BOND IN UNITS SURVIVING FREEZING AND THAWING TESTS

As stated previously, the units that survived the freezing and thawing tests were also tested for strength of bond. The results are given in Table 14. These averages include all units not loaded, made with 1 : 1 : 6 mortar, and stored under all three conditions for two months prior to undergoing the freezing and thawing tests.

TABLE 14.—*Strength of bond in units surviving freezing and thawing tests (1 : 1 : 6 mortar, with and without lugs)*

Brick	Number of units tested	Average strength of bond
		Lbs./in.²
No. 1	12	45.1
No. 2	3	27.6
No. 3	20	29.1
No. 4	8	23.0
No. 5	21	22.7

The average strength of bond for those units made with brick Nos. 1 to 4, inclusive, which survived the freezing and thawing tests compares favorably with similar data for the same brick, but for units not subjected to freezing and thawing as given in Table 10. Since all of the units formed with brick No. 5 were subjected to freezing and thawing tests, data of the kind given in Table 10 were not obtained for this brick.

This comparison shows beyond a doubt that the bond failure was not due to disintegration of mortar. Had such been the case, the

average values in Table 14 would be less than the averages given in Table 10. This was also evident from visual inspection. There was no visible disintegration, chipping, or spalling of either brick or mortar during these tests.

(g) STRENGTH OF BOND AS RELATED TO MORTAR

Table 15 presents a summary of the results obtained with all of the survivors of all of the units made from brick No. 5.

TABLE 15.—*Strength of bond as related to mortar used (units loaded and not loaded, with and without lugs)*

Mortar	Units loaded					Units not loaded				
	Total number of units made	Number of survivors tested for strength	Strength			Total number of units made	Number of survivors tested for strength	Strength		
			Average	Individual maximum	Individual minimum			Average	Individual maximum	Individual minimum
			Lbs./in.²	*Lbs./in.²*	*Lbs./in.²*			*Lbs./in.²*	*Lbs./in.²*	*Lbs./in.²*
1:3	108	76	27.3	84.0	1.9	108	37	31.3	69.9	5.4
1:1:6	108	63	15.5	71.6	2.0	108	21	22.7	60.9	7.4

The data indicate that the strength of bond in units which survived the 50 freezing and thawing cycles was not measureably improved by loading.

With reference to the units described in Table 15 it may be mentioned that, when those bonded with 1:3 cement-sand mortar were pulled apart, but very little mortar remained on the top brick in practically all cases. The fracture was largely one of bond failure, occurring at the junction of the mortar and the upper brick. This was true regardless of whether or not the units had been loaded. However, in the case of 1:1:6 mortar units which were loaded, this was not the case. After the brick in these loaded units were pulled apart, as much mortar was adhering to the upper as to the lower brick in most cases; actually, it was the tensile strength of the mortar rather than the strength of bond that was measured. Among units not loaded and made with 1:1:6 mortar, the mortar usually adhered more or less over the entire surface of the upper brick, but was less in amount than that clinging to the lower brick. This last statement applies also to units made from brick 1 to 4, inclusive, and to both those units which were and those which were not subjected to freezing and thawing. This means briefly that the ratio, strength of bond to tensile strength of mortar, was greater in 1:1:6 than in 1:3 mortar.

IV. CONCLUSIONS

1. The above data indicate that failure of bond between mortar and brick, under the conditions described, was not due to disintegration of either brick or mortar.

2. Dense impervious brick which absorb water very slowly can be bonded satisfactorily with mortar.

3. Under the same or nearly the same conditions, the strength of bond attained by using relatively porous brick tended to be slightly greater than that characteristic of units formed with relatively impervious brick. However, in so far as durability of bond (as determined in the manner described) is concerned, the absorption properties of the brick were not of any considerable importance when due regard was given to the necessity of thoroughly wetting the rapidly absorbing brick.

4. With good workmanship, there were other considerations which in their effect on the bond durability were of more importance than the absorption properties of the brick. These were: The amount of pressure which the mortar bed sustained during the tests, whether or not the brick were free to move so as to tend to reduce stresses induced by shrinkage in the mortar; and the type of mortar that was used.

5. There was nothing to be gained either from the standpoint of strength or of durability of bond by wetting brick which did not wet through from edge to edge within less than 4 hours time.

6. The ratio, strength of bond to tensile strength, was greater in 1:1:6 than in 1:3 mortar.

7. There was a slightly greater percentage of failures of bond with the 1:1:6 than with the 1:3 mortar.

8. The percentage failures of the nonloaded units was twice that of the loaded ones. This may be interpreted as indicating that bond failure is most likely to occur in vertical joints in masonry. It would be well to have an absolute minimum of such joints and to adequately protect them from moisture as much as possible in order to avoid excessive water penetration through cracks formed between the masonry units and the cementing material.

9. There were appreciably more bond failures when metal lugs were embedded in the mortar joints than there were when such were omitted. It was intended in this procedure to simulate in one-half of the units, conditions whereby the brick could not be drawn nearer together as the mortar shrunk. Such a condition apparently exists sometimes in vertical joints in masonry.

10. These data suggest the necessity of continuing studies of all types of masonry materials and broadening their scope in order that, ultimately, mortar and building units generally may be better adapted to one another and that the life of the bond in exposed places in all masonry construction may be materially increased.

V. ACKNOWLEDGMENTS

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HEAT TRANSFER THROUGH BUILDING WALLS

By M. S. Van Dusen and J. L. Finck

ABSTRACT

A method for measuring the heat transfer through large flat slabs, such as wall sections, is described in detail. The method requires no actual measurement of heat flow over large areas and no accounting for inevitable losses in undesired directions, except where lateral losses may occur by radiation, but consists in comparing the thermal resistance of an unknown panel with a standard, the resistance of which can be accurately determined by the hot-plate method, by which the measurement of heat flow is made under much more favorable conditions.

Results on 17 walls are given. The accuracy of the measurements is of the order of 5 per cent in the apparatus described. Greater accuracy than this can only be attained by better control of conditions, which becomes increasingly difficult as the temperature variation limits are narrowed. Such refinements would seem to be superfluous, however, in view of the degree of reproducibility of such structures as building walls.

In addition to the above, results are also given for five small panels, these observations being made with a hot plate 24 inches square. These smaller panels consisted of certain individual components of frame wall construction.

An analysis of the data permitted the calculation of the conductances and resistances of the various components entering into the construction of ordinary types of walls. These values are presented in tabular form, and their use permits the calculation of the resistance (or conductance) of any combination of the various components for which data are given. The resistances of a number of wall combinations were calculated and compared with the data of other experimenters. The agreement is, in general, fairly satisfactory.

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I. INTRODUCTION

The heat transfer through building walls has been the subject of considerable investigation in the past, but the wide discrepancies in existing data seem to warrant further investigation, at least to the point where the heat transfer through the more common types of exterior walls can be estimated with a fair degree of approximation. This has been possible in the case of the walls of cold-storage buildings where a considerable thickness of insulating material is applied, since the thermal conductivity of the latter class of materials is either known or easily measured, and the structural portions of the wall contribute relatively so little resistance to heat flow that their thermal properties need only be very roughly known. Ordinary building walls, however, present a different problem, and it is not feasible, in many cases, to calculate the heat transfer from a mere knowledge of the thermal conductivities of the various materials composing the wall, although such a procedure is not theoretically impossible. In fact it is very desirable to proceed in this direction as far as possible, even with our present incomplete knowledge of data of heat transfer, since it results in a large reduction in the number of separate experiments required to obtain working data on a large number of combinations.

Building walls can be reproduced with only a fair degree of approximation; consequently it is of no particular value to attempt to measure the thermal properties of a single specimen with much greater accuracy than this type of construction is ordinarily reproduced. The degree of reproducibility, however, is difficult to estimate, and varies greatly with the type of wall, character of workmanship, etc.; consequently it is practically necessary to choose some reasonable limits of error and attempt to keep within them.

The present paper gives the results of an investigation pertaining essentially to the development of a practical method for measuring the heat transfer through building walls under laboratory conditions which can be reproduced and controlled. Measurements were made on some of the more common types of walls used in the construction of buildings.

II. PRINCIPLES OF HEAT TRANSFER THROUGH WALLS

1. HEAT FLOW UNDER STEADY CONDITIONS

The steady flow of heat through a wall by reason of a constant temperature difference between the surroundings on the two sides depends upon four partially independent processes, (1) the transfer of heat to the wall from the surroundings on the hot side, (2) the transfer through the wall, (3) the transfer of heat to the surroundings on the cold side, and (4) the diffusion or flow of air through the wall in either direction. Neglecting for the present the effect of possible air leakage, let us first discuss, in general, the other three processes or factors mentioned above.

The total resistance to heat flow through the wall is the sum of the resistance of the wall itself and the two resistances between the surfaces of the wall and their respective surroundings. The thermal resistance per unit area may be defined quantitatively as the number of degrees temperature difference required between the boundaries of the system

(surfaces or surroundings, as the case may be) to produce unit rate of heat flow through unit area, the direction of flow being normal to the area. The reciprocal of the resistance per unit area of a system of solid materials in layers is the conductance per unit area, defined as the rate of heat flow through unit area produced by a temperature difference of 1° between the boundaries of the system. It will also be convenient to speak of two other quantities, viz, thermal conductivity and transmittance per unit area. Thermal conductivity is a property of a homogeneous material, and is defined as the rate of heat flow through unit area when the temperature difference perpendicular to the area is 1° per unit thickness. Transmittance is a term applied to the over-all heat transfer from air to air, and is therefore the reciprocal of the total resistance from air to air.

The values of the quantities defined above are not strictly constants but vary with the mean temperature and the temperature difference, but the variations are small and for the present these quantities will be treated as constants for the sake of simplicity and clearness. If necessary any variations in them can be taken into account in the solution of actual problems.

2. SURFACE RESISTANCE

The resistance to heat flow between the surface of a wall and its surroundings is ordinarily called surface resistance, although it is only partially dependent upon phenomena taking place at the surface of the wall. The transfer of heat takes place by all the modes of heat transfer, viz, conduction, convection, and radiation, and the relative contribution of each depends upon the conditions. Heat is transferred from the air to the wall, or vice versa, by convective air currents set up by temperature differences between wall and air, by wind or forced ventilation. At points very near the wall the velocity of the air is reduced; the motion becomes approximately streamline, and heat is transferred from these regions to the solid surface of the wall mainly by pure conduction through layers of air moving parallel to the wall, and therefore not transferring heat to it by turbulent motion. Some convection, of course, occurs even fairly near the surface. For a constant mean velocity of moving air, the heat transferred between air and wall will be very nearly proportional to the temperature difference, or, in other words, the surface resistance due to air only will be a constant, and independent of the temperature difference. The resistance will, however, decrease greatly with increased air velocity. In the case of natural convection, the air velocity increases with increasing temperature difference; consequently, the surface resistance will decrease with increasing temperature difference, and may be regarded as depending only upon the temperature difference and the mean temperature. The variation of the resistance with the mean temperature is too small to be of much importance in this connection, but the variation with air velocity is important, since in a moderate breeze the resistance is reduced to a very small value relative to the total resistance of the wall.

In addition to the heat transferred by convection and conduction in the air, an entirely independent transfer takes place by radiation between the surface of the wall and its surroundings. The magnitude of such transfer depends on the absolute temperature, the temperature difference, and the character of the surfaces of the wall and surround-

ings. If the wall and its surroundings had reflecting surfaces of clean, bright metal, the interchange of heat by radiation would be very small at ordinary temperatures. In all practical cases, however, the surfaces are nonmetallic, and the transfer of heat by radiation is usually somewhat greater than the convective transfer, even at ordinary temperatures. Furthermore, the radiating and absorbing properties for the kind of radiation emitted at ordinary temperatures are practically the same for any materials likely to be found either on the wall surface or on the surroundings. The heat interchange by radiation may, therefore, be considered as dependent only on the temperatures in almost all practical cases. For moderate temperature differences, the heat transfer by radiation is proportional to the product of the temperature difference and the cube of the absolute temperature. The variation with the absolute temperature amounts to about 1 per cent per °C. at ordinary temperatures, but this variation, although considerable, is not of much importance in dealing with the total thermal resistance of a wall.

The surface resistance is the numerical measure of the complicated combination of all the effects of conduction, convection, and radiation. It is ordinarily defined as the temperature difference between the solid surfaces of the wall and the surrounding air required to produce unit rate of heat flow per unit area of wall surface. The air temperature is supposed to be measured at sufficient distance from the wall surface such that the effect of the wall is inappreciable. Strictly speaking, such a definition can only apply if all the surroundings are at the same temperature as the air, since the transfer of heat by radiation is independent of the air temperature, except in so far as the air influences the temperature of the surroundings.

3. WALL RESISTANCE

The thermal resistance of the wall itself is separate and distinct from the surface resistances. It is a property of the wall and is not influenced by the surroundings except in certain cases of air leakage which will be noted later. Heat transfer through solid walls takes place only by conduction in the direction of temperature gradients. Such transfer is proportional to the temperature difference between the two surfaces of the wall and further depends on the materials composing the wall. The thermal conductivities of building materials in general, increase slightly with increasing temperature; consequently the resistance of a wall will decrease somewhat with increasing mean temperature of the wall.

Heat transfer through walls containing voids, such as hollow tile, frame, or the hollow types of brick walls, takes place by convection and radiation as well as conduction. The resultant process is very complicated in any ordinary type of hollow-wall construction, and it is at present difficult to separate the three effects and ascertain which one plays the most important rôle in any particular type of construction. Our knowledge of the heat transfer in inclosed air spaces is limited at present, but it may be said, in general, that such transfer will increase with the temperature by significant amounts due primarily to the large variation in radiation. Walls of this nature are subject to much greater variation in construction than solid walls, since more or less mortar is forced into air spaces, depending upon chance and the individual workman.

4. HEAT TRANSFER BY AIR INFILTRATION

Aside from conduction, convection, and radiation, an entirely independent transfer of heat may take place by infiltration of cold air through the wall on the windward side of a building, with the consequent efflux of warmer air on the lee side of a building. In an extreme case, air infiltration may be so large as to cause material change in the temperature gradient in the wall, and, therefore, influence the outward heat flow by conduction. No discussion of such an extreme case, however, will be made here.

The magnitude of the effects of air infiltration through walls has been investigated in recent years by Houghten and Ingels,[1] and also by Larson, Braatz, and Nelson,[2] and the general conclusion seems to be that infiltration through plastered and finished walls plays, on the average at least, a very minor rôle in the heat loss from buildings. It must be remembered, however, that all the measurements referred to are concerned directly with air flow through the wall by reason of pressure differences; no direct measurements of heat transfer under conditions of wind pressure having been made. It is evident that an impermeable layer at any place in the wall will entirely eliminate air infiltration to the interior, but not necessarily annul the effects of partial air penetration on the total heat loss through the wall. If the relatively impermeable (to air) layer is on the inside of the wall (as it usually is), the possibility of penetration of cold air part way into the wall and out again must be recognized. If the outward path for air flow is directly against the wind pressure causing the penetration, it is to be expected that a sort of equilibrium will be maintained, with little or no heat transfer by air movement. On the other hand, if there is an open path for air flow into an air space on the windward side and out at some point at lower pressure, for example the attic or the lee side, the resulting effect will be a heat loss from the building. The magnitude of such effects is on the average wholly problematical, but probably not very great. In certain individual buildings, however, the effect is undoubtedly large. Obviously, walls containing air spaces should be protected as well as possible on the outside against air infiltration.

5. HEAT FLOW UNDER VARIABLE CONDITIONS

When the temperature of any or all points in the system considered varies with time, certain other factors enter into the problem of heat flow through a wall. It is evident that the variable condition is the only one which actually occurs in practice, not so much on account of the small rapid variations in temperature, but rather to the large variations from day to night. As the air temperature and external wall surface temperature fall rapidly during the night, heat flows outward from the wall at a greater rate than it flows into the wall from the inside. The flow of heat into the outside air is maintained at the expense of heat stored in the wall, and it is only when this store is exhausted that a steady state is again established. In a thick wall with large heat capacity it may require several days for the steady state to become approximately established; consequently, by morning

[1] J. Am. Soc. Heating and Ventilating Eng., **33**, pp. 249–258; 1927.
[2] J. Am. Soc. Heating and Ventilating Eng., **35**, pp. 125–132; 1929.

that portion of the wall near the inside of the building is still losing heat at practically the same rate as it was the night before. The morning rise in temperature on the outside then tends to counteract the cooling of the previous night, the outer portions of the wall store up the heat lost the night before, and the inside portions of the wall, and consequently the net outward heat flow from the interior, remain practically unaffected from day to day, provided the same temperature conditions are repeated. Slower variations in temperature, however, such as cold or warm waves extending over a period of several days, have time to penetrate to the inside surface of the wall, and their effects are consequently felt.

The net outward heat flow, however, in the case of uniform periodic variation in outside temperature is the same as it would be if the outside were kept at some uniform mean temperature between the maximum and minimum outside temperatures.

Suppose we consider two walls, each having the same thermal resistance (measured in a steady state), but different heat capacities, such as a solid wall and a wall made up of air spaces and paper. Under the same steady conditions the heat transfer through each will be the same. Under the same varying temperature on the outside, the net heat flow integrated over a complete period will still be the same, but a different procedure must be followed in each case to maintain the inside at constant temperature. In the case of a thick solid wall, a constant heat supply will accomplish this object, assuming that the period of the fluctuation of the outside temperature is equal to 24 hours. With the air-space wall, however, more heat must be furnished to the inside during the night than during the day, since such a wall as we have assumed has very little heat capacity.

If the object is to maintain a fairly uniform temperature indoors at all times, the solid wall has a certain obvious advantage over the wall with small heat capacity, although the consumption of fuel in each case is the same if the same temperature conditions are maintained.

We have here considered two extreme cases for the sake of example. In actual practice, the differences between two walls having the same resistance are much less and probably not of very great importance in heating during cold weather. In summer, however, on sides exposed to the sun, walls having large heat capacity tend to keep the building cooler during the hot part of the day.

III. EXPERIMENTAL ARRANGEMENTS AND METHODS OF TEST

The main object of the present series of measurements has been to compare the thermal resistance of various types of walls under reproducible and constant conditions. These conditions have been arranged in such a way that no appreciable effects due to air leakage or moisture would seem possible. A comparison of this kind will apply equally well to a condition of variable temperature such as actually occurs in practice, but evidently will not be valid if air leakage enters as a significant factor in actual use. It seems more feasible, however, to determine air leakage separately, in terms of mass of air rather than in quantity of heat.

The surface resistances on the two sides are not of particular importance in the laboratory comparison of the walls themselves, since, as noted previously, they are not dependent upon the walls, but rather upon conditions external to the walls. Any incidental measurements of the surface resistances, however, will be of value, although difficult to apply under service conditions.

In the present series of experiments, the method is to maintain as nearly as practicable a constant temperature difference between circulating air on the two sides of a system composed of a specimen wall panel in contact with another panel of known thermal resistance. The two panels may be considered in series, and therefore the same heat flows through both. Let

H = heat flow in B. t. u. per hour, per square feet area.
t_1 = temperature in °F. of the warm surface of the panel to be tested.
t_2 = temperature in °F. of the cold surface of the panel to be tested.
t_3 = temperature in °F. of the warm surface of the known panel.
t_4 = temperature in °F. of the cold surface of the known panel.
C = conductance per unit area for the panel to be tested.
C_0 = conductance per unit area for the known panel.

Then

$$H = C\,(t_1 - t_2) = C_0\,(t_3 - t_4) \tag{1}$$

and

$$C = C_0 \frac{t_3 - t_4}{t_1 - t_2} \tag{2}$$

As will be described below, the temperature difference between the surfaces of the known panel are measured by a multiple-junction thermocouple. This panel is calibrated in a hot-plate apparatus. If

E = e. m. f. in millivolts of the multiple-junction thermocouple when the temperature difference is $t_3 - t_4$.
K = heat flow through the known panel in B. t. u. per hour, for an e. m. f. of 1 millivolt.

then

$$C_o\,(t_3 - t_4) = KE \tag{3}$$

and

$$C = K \frac{E}{t_1 - t_2} \tag{4}$$

The resistance per unit area, R, is given by the equation

$$\mathrm{R} = \frac{1}{C} = \frac{t_1 - t_2}{KE} \tag{5}$$

To calculate surface resistance, let
t_a = temperature in °F of the air several inches from the surface.
t_s = temperature in °F of the surface.
r = surface resistance per unit area.
If t_a is greater than t_s, we have

$$r = \frac{t_a - t_s}{KE} \tag{6}$$

and if t_s is greater than t_a

$$r = \frac{t_s - t_a}{KE} \tag{7}$$

This method of comparison was chosen, rather than a direct measurement of heat input, because of the great difficulty in accounting for all the heat generated on the warm side of the system. The comparison panel, on the other hand, is comparatively thin and easy to calibrate in another apparatus of known reliability.

1. APPARATUS

A diagrammatic sketch of the cross section of the apparatus used is shown in Figure 1. It consists of two insulated chambers each

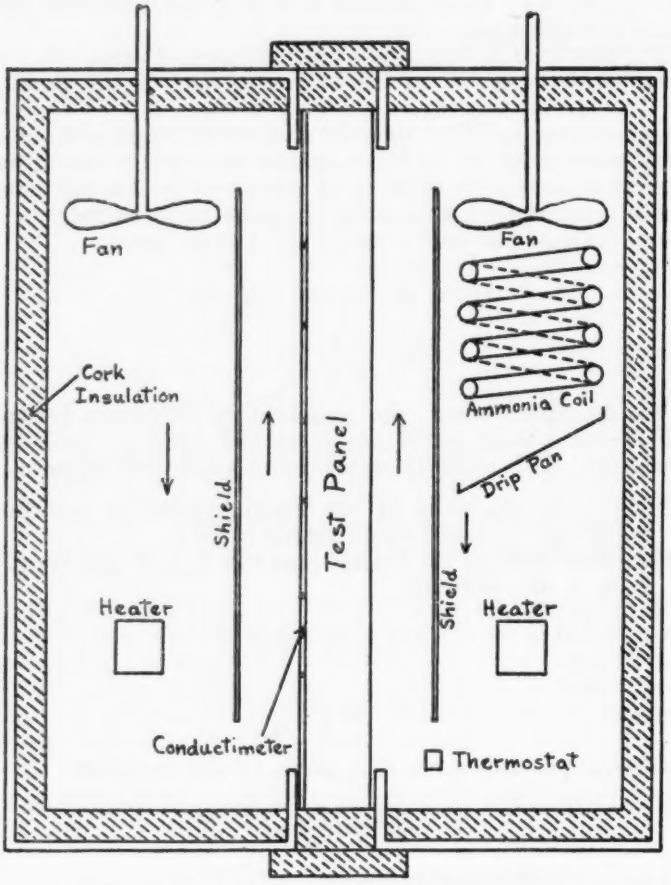

FIGURE 1.—*Diagrammatic sketch of apparatus*

open on one side, serving as the means for maintaining a temperature difference between the two sides of a wall panel placed between them. The wall panel forms a common wall on the otherwise open side of each chamber. By means of steel rods the two chambers are clamped against the panel with considerable pressure, and effectively sealed by felt gaskets. The right-hand chamber is kept at the lower temperature and is equipped with an ammonia expansion coil, an electric heating coil, a thermostat, and a fan for air circulation and heat

FIGURE 2.—*Apparatus disassembled*

1, Test wall; 2, conductimeter; 3, cooling coil; 4, heater; 5, thermostat; 6, cold chamber; 7, warm chamber.

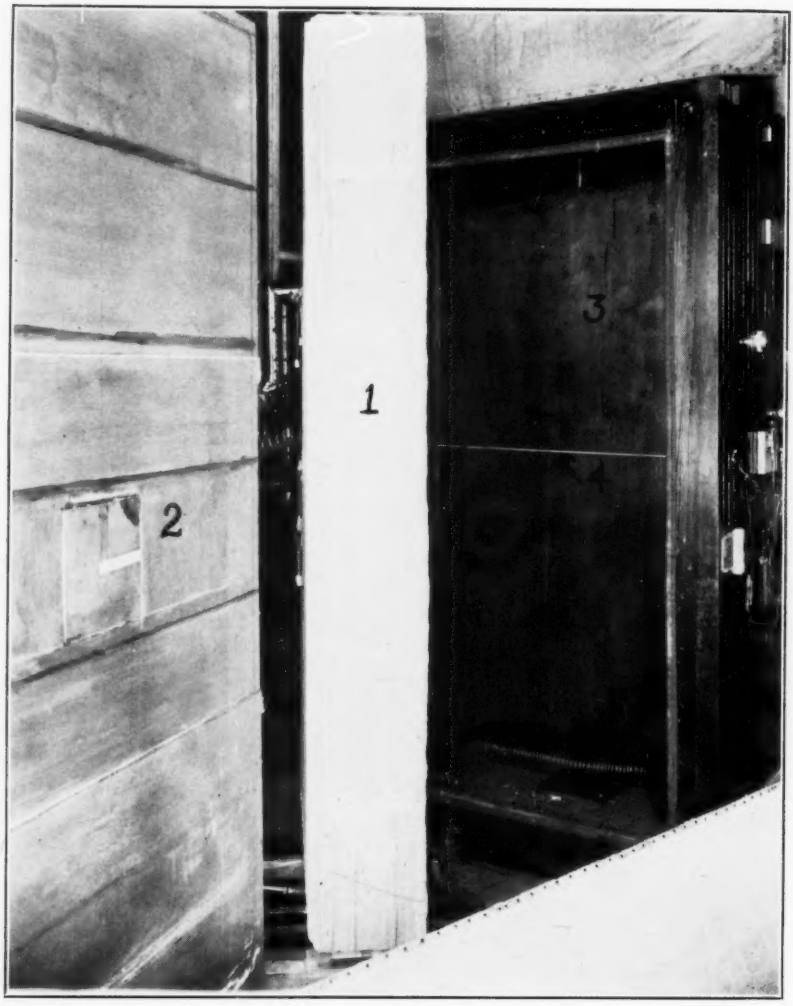

FIGURE 3.—*Apparatus partly assembled*

1, Test wall; 2, conductimeter; 3, shield in cold chamber; 4, thermocouple which measures the cold in temperature.

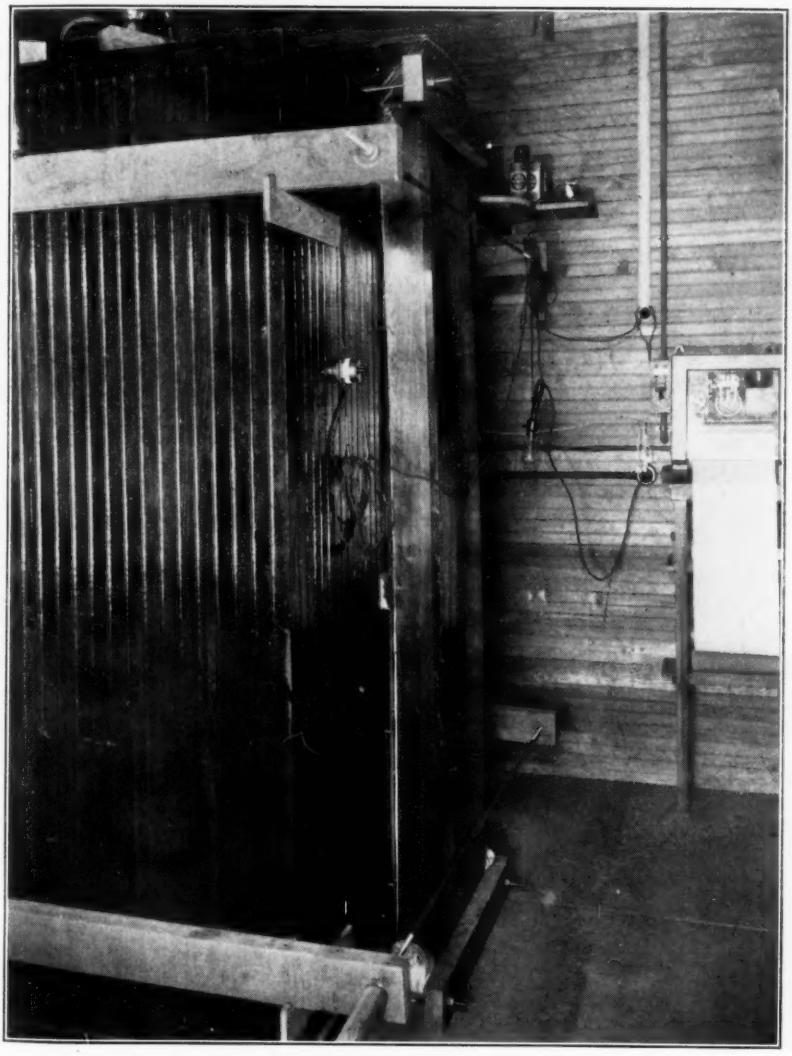

FIGURE 4.—*Apparatus completely assembled*

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distribution. These accessories are labeled in the sketch and are also shown in Figures 2, 3, and 4 (photographs of the apparatus in different stages of assembly). The chamber is refrigerated by means of a three-fourths-ton automatic refrigerating machine, located outside the test room. The machine is equipped with a bimetallic thermostat (shown in fig. 2) for automatically starting and stopping, but this form of control was not used, since it did not give close enough regulation. The actual method of operation was to keep the machine running all the time, the ammonia back pressure in the expansion coil being maintained constant by an automatic throttle valve. The supply of refrigeration was, therefore, approximately constant and the small fluctuations in it were balanced by heat supplied electrically and controlled by another thermostatic device.

It was later found necessary to move the entire apparatus into another room, and refrigerated brine was used instead of ammonia, employing, however, the same cooling coil. The same procedure was followed with the brine; that is, allowing the brine to flow through the coil at whatever temperature it was delivered, and balancing this against heat supplied electrically and controlled by a thermostatic device.

The thermostatic device consists of a coil of copper tubing filled with toluene and connected to a U tube containing mercury to make and break an electric contact. The U tube is mounted on the outside of the chamber. By this method of operation the mean temperature of the cold chamber could be kept constant to about 0.5° C., although the lag of the system distributing the heat caused the periodic fluctuations due to the make and break of the thermostat to be considerably larger than this. The period of these fluctuations, however, was usually less than one minute, and their effects were consequently not appreciable on the wall surface. It was necessary to run the fan at a fairly high speed in order to maintain a uniform temperature distribution over the test panel. The average velocity of the air in the space between the panel and shield was roughtly measured with a small vane anemometer and found to be of the order of 5 miles per hour. Under these conditions the temperature distribution in the air stream was uniform to a few tenths degree at all points more than about 1 inch from the surface of the panel, and over most of the area of the latter. This distribution was determined by a large number of thermocouples distributed at various points in this region.

A thin wall-board shield, with openings at top and bottom, is mounted, as shown in the figure, 6 inches from the surface of the test panel and serves to direct the air circulation from the fan up and along the face of the test panel, as well as to shield the latter from the direct influence of the cooling and heating coils.

The warm chamber is identical with the cold chamber except that it contains no cooling arrangement and no thermostat. The latter is not necessary, since a constant current from a storage battery is supplied to the heater, and all the surroundings are in a steady state. The temperature of the hot chamber can be varied by varying the current supplied to the heating coil.

The room in which all the apparatus except the refrigerating machine is located is a small insulated interior room, the temperature of which is automatically controlled by a thermostat similar to the one in the cold chamber. The temperature of the room is ordinarily

maintained a few degrees above the rest of the building, so that no cooling is required, and only a small amount of heat supplied electrically.

2. CONDUCTIMETER

The comparison panel, or conductimeter, as it has been termed, consists of a thin panel of homogeneous material whose thermal conductivity is known. Two types of conductimeters were constructed. The first was made of clear white pine about three-fourths inch thick. For convenience, and to insure better thermal contact with the test panel, it was built in three sections, each about 3 by 2 feet, the edges being bound with strips to prevent warping, and the whole panel well varnished. No apparatus being available for the calibration of such a large panel, an opening 8 inches square was cut from the center and a calibrated piece of the same material inserted. The construction and calibration of this latter piece will be considered more in detail later.

A second conductimeter was made of a cork composition [3] one-fourth inch thick. This was also built in three sections 3 by 2 feet, and the surfaces were well varnished. An opening 8 inches square was cut from each of these sections, and a calibrated piece of the same material inserted. The advantage that this second conductimeter has over the first is that it is somewhat flexible, and by exerting pressure at various points over the surface a far better contact may be had with the test panel than can be obtained with the white pine conductimeter. In employing the cork conductimeter provision was made in the hot chamber, by means of wooden pegs and springs, to press the conductimeter against the panel.

In the construction of the center piece of white pine, two pieces of clear fine-grained white pine (pattern lumber) each 8 inches square and about one-fourth inch thick were glued together with their grain at right angles to form a permanently flat piece about one-half inch thick. Twenty-five thermocouples in series were mounted on the two sides of the board, the junctions being placed alternately on one face and the other and distributed uniformly over the surfaces. No. 36 copper and constantan wire were used for the couples, the junctions being silver soldered, and the two wires from each junction being led along the surface of the board for about an inch before being threaded through fine holes in the board. A piece of veneer was then cemented to each side of the board with soft deKhotinski cement and the conductimeter placed in a press while the cement was still soft.

The center pieces of cork were made of the same material as the rest of the conductimeter. Thermocouples made of No. 32 copper and constantan wire, five in number, were distributed evenly over each surface of the piece, and were connected in series. The surfaces were then varnished and thin tin foil was pasted over them. The purpose of the foil was to insure constancy in the composition of the material, for it was suspected that the content of moisture or other volatile material might vary over a long period of time and change the calibration.

In each of the two conductimeters, the center piece had a number of couples in series, since it was intended to use a rather insensitive instrument, such as a potentiometer recorder or a portable potenti-

[3] A cork composition made by the Armstrong Cork Co., known under the name of "Suberac."

ometer indicator to make the e. m. f. measurements. Each of these pieces was calibrated in a thermal conductivity apparatus described elsewhere.[4] This apparatus is designed for two identical test specimens, consequently for the white-pine section it was necessary to use a slab of material of known conductivity on one side of the heating plate and calculate the heat flow through this specimen. A slab of cork board, the conductivity of which had been precisely determined, was used for this purpose. Four center pieces of the cork composition were constructed, and they were calibrated in pairs without the aid of any other material.

Calibrations were made in this apparatus at different times. Check calibrations were made under conditions of actual use by the following method: A panel was constructed of cork board, whose thermal conductivity and thickness were known. This panel was used in conjunction with the conductimeters, and a regular test was made in the large apparatus similar to a test on walls. The following results were obtained:

Average thickness of cork panel = 1.222 inches.

Thermal conductivity (determined in hot-plate apparatus) = 0.29 B. t. u. hr.$^{-1}$ ft.$^{-2}$ deg.$^{-1}$ F. in.

Conductivity of cork panel as determined by conductimeter at—

Date	Top	Middle	Bottom
Oct. 19, 1927	0.31	0.32	0.31
Oct. 21, 1927	.27	.29	.29
Dec. 13–16, 1927	.28	.30	.29

These results indicate a satisfactory accord of the methods employed.

3. WALLS [5]

No. 1. 8-inch brick wall.—Surface clay (Baltimore) brick; American bond (headers every sixth course); plaster on one side; workmanship is of such nature that all joints (vertical and horizontal) are completely filled with mortar; built by mason A. Total thickness, 8⅞ inches. See Figures 5 and 6.

The mortar of this and all other walls consists of 1:1:6 Portland cement, hydrated lime, sand, by volume. The plaster of all walls consists of scratch and brown coats of 1:3 gypsum plaster (fibered) and sand; finish coat consists of 1:1 hydrated lime and calcined gypsum.

No. 2. 8-inch brick wall.—Very hard burned (New England) brick, formed from dense surface clay; American bond; plaster on one side; workmanship similar to wall No. 1, but built by mason. B. Total thickness, 8⅞ inches.

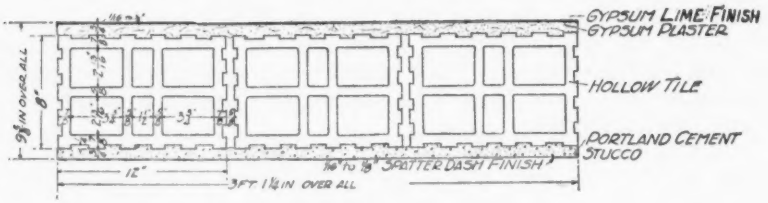
No. 3. 8-inch brick wall.—Rather porous, dry-pressed (Mississippi) brick, formed from surface clay; workmanship same as for wall No. 2. Total thickness, 8⅞ inches.

[4] Van Dusen, J. Am. Soc. Heating and Ventilating Eng., October, 1920; Am. Soc. Refrigerating Eng. J. November, 1920.

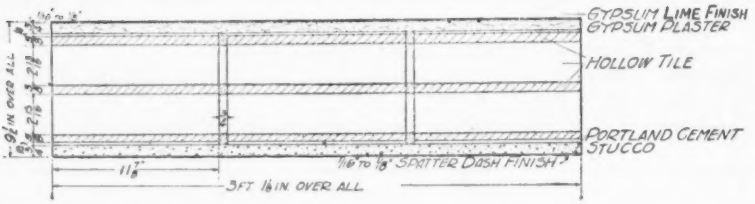
[5] Three masons, A, B, and C, were employed in the construction of these walls. Masons B and C are the same as those employed in the construction of the walls for Research Paper No. 108, B. S. Jour. Research. The workmanship of mason A is similar to that of B. For a more complete description of the walls built by masons B and C the reader is referred to the above-cited paper.

No. 4. 12-inch brick wall.—Mississippi brick; same as wall No. 3, except that the total thickness is 13¼ inches.

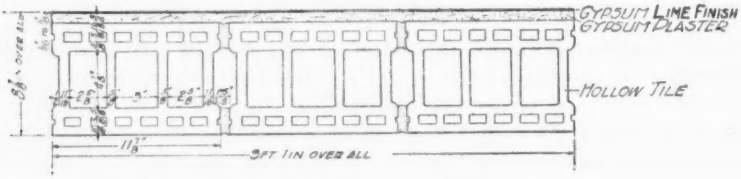
No. 5. 8-inch brick wall.—Mississippi brick; differs from wall No. 3 in that the workmanship is characterized by furrowed horizontal



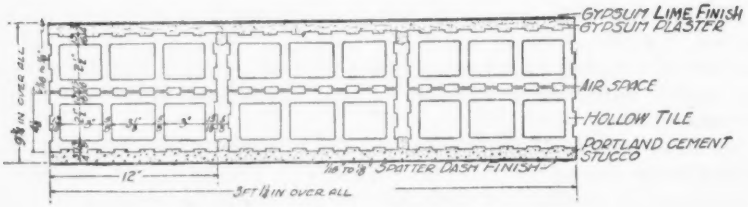
8-INCH HOLLOW TILE WALL (END CONSTRUCTION)



8-INCH HOLLOW TILE WALL (SIDE CONSTRUCTION)



8-INCH HOLLOW TILE WALL (DOUBLE SHELL)



8-INCH HOLLOW TILE WALL (TWO UNIT)

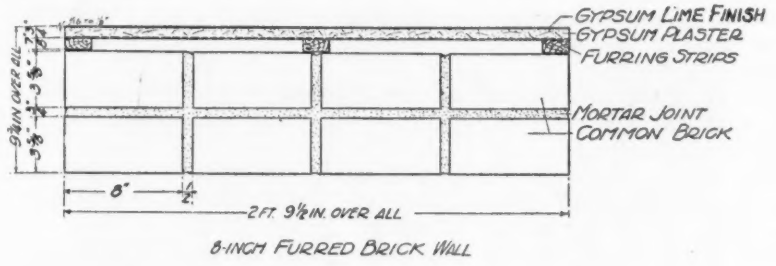
FIGURE 5.—*Horizontal cross section of test walls*

joints (see fig. 7), and unfilled vertical longitudinal joints. (See fig. 8.) Built by mason C. Total thickness, 8⅞ inches.

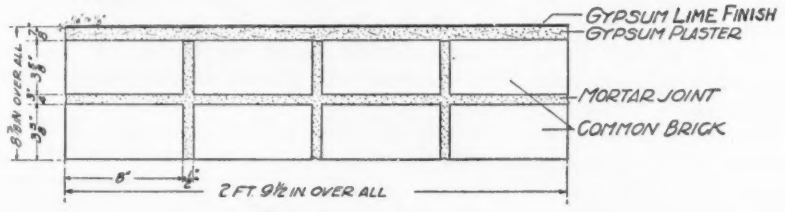
No. 6. 8-inch furred brick wall.—Baltimore brick; workmanship same as for wall No. 1. Furring consists of seven-eighths inch wood strips covered with expanded metal lath, making a total thickness of

10 inches. Built by mason A. Total thickness 9¾ inches. (See figs. 5 and 6.)

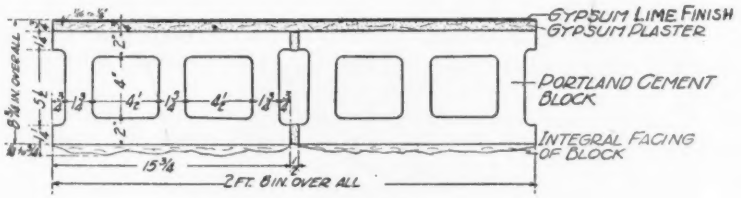
No. 7. 8-inch rolokbak wall.—Mississippi brick; built by mason B; plastered on one side. Total thickness 8⅞ inches. (See fig. 9.)



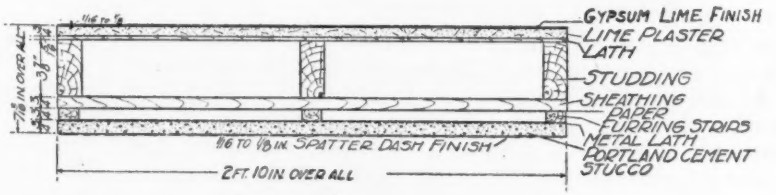
8-INCH FURRED BRICK WALL



8-INCH BRICK WALL



8-INCH CEMENT BLOCK WALL



FRAME WALL

FIGURE 5.—*Horizontal cross section of test walls*—Continued

No. 8. 8-inch all-rolok wall.—Materials and workmanship same as for wall No. 7. Total thickness 8⅞ inches. (See fig. 10.)

No. 9. 8-inch all-rolok wall.—Baltimore brick; built by mason A; otherwise similar to wall No. 8.

No. 10. 8-inch hollow tile (end construction).—8 by 12 by 12 inch XXX load-bearing, dense fire clay tile, set with cells vertical; inside, plastered; outside, stucco; total thickness 9⅝ inches. (See figs. 5 and 11.)

Outside surface consists of scratch coat of 1:1/10:2½ Portland cement, hydrated lime, and sand; stucco coat of same composition. This last coat is what is known as spatter dash, giving a very rough surface.

No. 11. 8-inch hollow tile (side construction).—Same as wall No. 10, but with tile set with cells horizontal. Total thickness 9½ inch. (See figs. 5 and 11.)

No. 12. 8-inch hollow tile (double shell).—5 by 8 by 12 inch dense fire clay, double shell, load bearing tile; cells vertical, and plaster on one side. Total thickness 8⅞ inches. (See fig. 5.)

No. 13. 8-inch hollow tile (two unit).—4 by 12 by 12 inch three-cell, dense fire clay, load bearing tile; set side by side with cells vertical; bonded with metal ties; plaster on one side, stucco on other. Total thikness 9¾ inches. (See fig. 5.)

No. 14. 8-inch Portland cement-sand block.—6 by 8 by 12 inch two-cell block, set with cells vertical, and plaster on one side. Total thickness 8¾ inches. (See fig. 5.)

No. 15. 4-inch frame.—Studs, 2 by 4 inches (actually 2 by 3⅝ inches), spaced 16 inches between centers; plaster on 5/16 by 1⅜ inch white pine lath; white pine sheathing, 13/16 by 11⅝ inches, spaced one-eighth inch apart, and covered with asphalt saturated roofing felt; furring strips, ¾ by 1½ inches, spaced 16 inches between centers, set vertically, forming an air space three-fourths inch width; stucco applied to expanded metal lath. Total thickness 7 5/16 inches. (See fig. 5.)

No. 16. 4-inch frame.—Same as wall No. 15, except that the stucco and furring strips were removed, leaving lath, plaster, 2 by 4 studs, sheathing and paper.

No. 17. Air space.—Air space formed by wooden frame; interior dimensions, 27⅞ by 65⅝ by 7 13/16 inches, the largest dimension being vertical; walls formed of compo wall board.

Data on compo wall board

Thickness of single sheet = 0.26 inch.
Conductance ..... = 2.63 B. t. u. hr.$^{-1}$ ft.$^{-2}$ deg.$^{-1}$ F.
Resistance ..... = .38.

The resistances of the two thicknesses of compo board have been allowed for in calculating the resistance of the air space.

All the panels were seasoned inside the building from two to four months before testing. During construction, copper-constantan thermocouples of No. 28 wire were placed at a large number of points in the interior, as well as on the surfaces of each panel. The inside surface of each panel was given a thin finishing coat of plaster to make the surfaces reasonably flat. The conductimeter panel was placed on the warmer side in contact with this surface, so that the irregularities of contact thermal resistance would be small.

4. OPERATION

The measurements of e. m. f. of the thermocouples were made with a portable potentiometer and a potentiometer recorder. The latter

FIGURE 6.—*View of brick walls Nos. 1 and 6 after test, showing character of workmanship*

FIGURE 7.—*View showing furrowed horizontal joints*

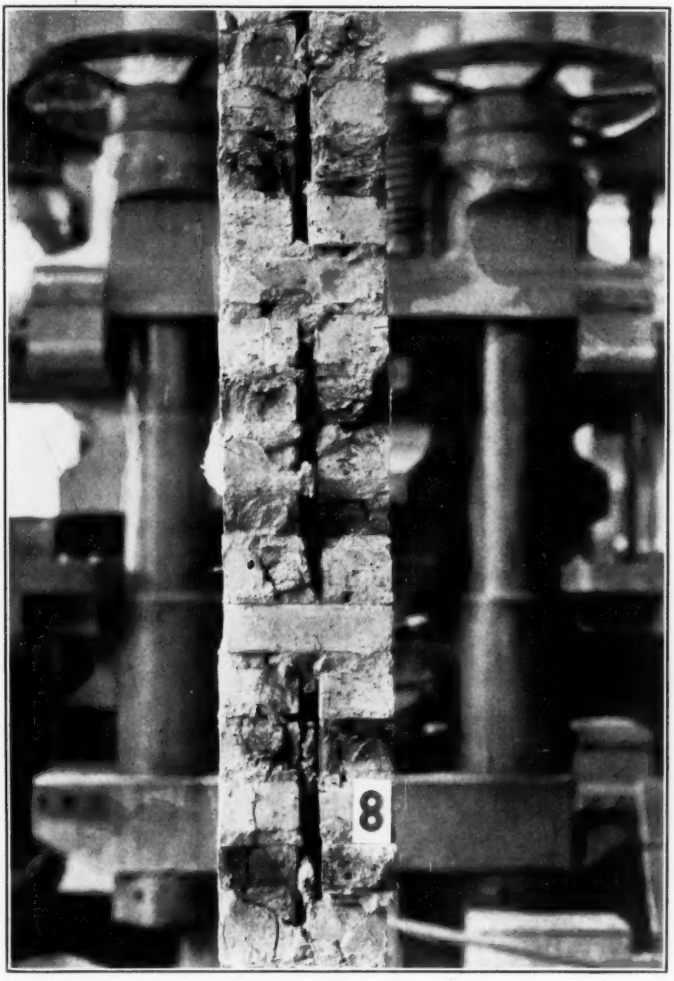


FIGURE 8.—*View showing unfilled vertical joints*

FIGURE 9.—*Wall identical with No. 7 in process of construction*

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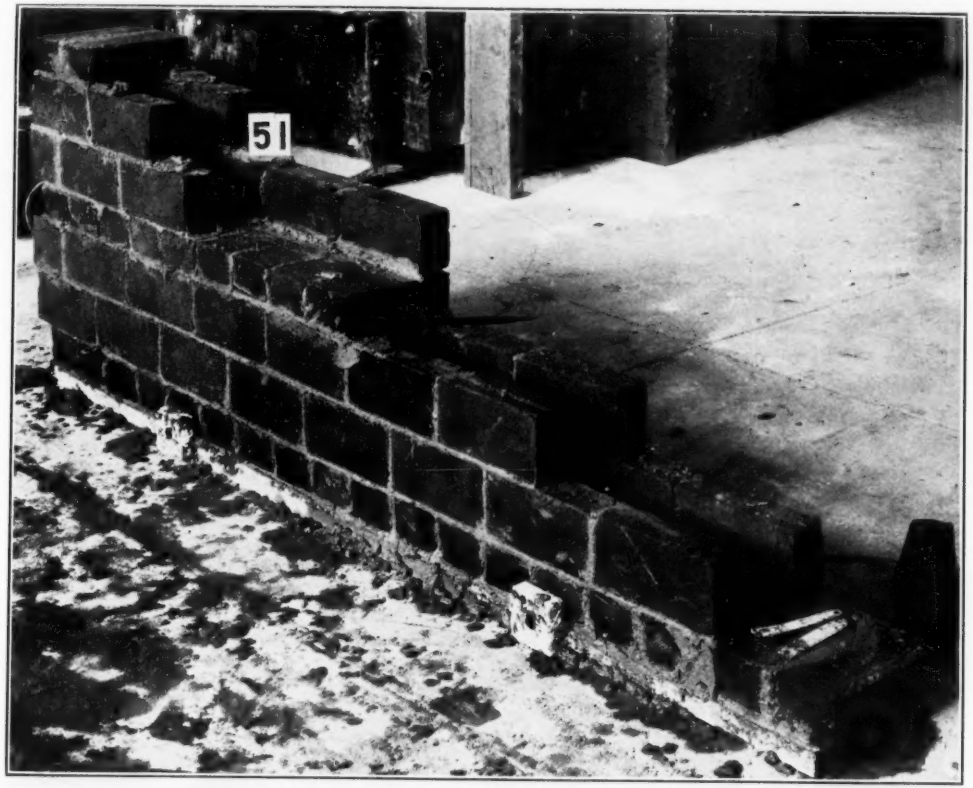

FIGURE 10.—*Wall identical with No. 8 in process of construction*

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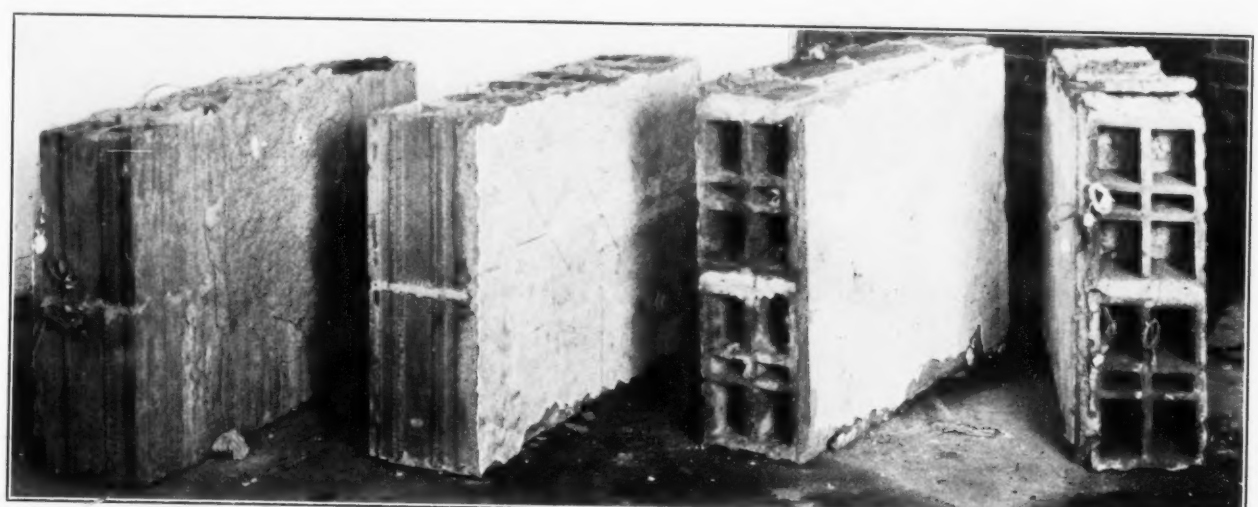

FIGURE 11.—*Walls Nos. 10 and 11 broken after test, showing character of workmanship*

was used only to indicate whether or not conditions had been steady during the night or between readings on the portable potentiometer. Readings could be made with an accuracy of about 0.02 millivolt, corresponding to about 1° F. on a single thermocouple. The regulation of temperature was not precise enough to warrant greater precision in reading. Most of the panels required about 48 hours to come to a sufficiently steady state, but the experiment was always continued more than two days if possible, in order to make certain that the system actually was in a steady state. It was found that large errors were likely to occur if the experimental conditions were not steady for long periods. A good many runs were terminated or disturbed by the accidental failure of one or more of the control devices. In many of these, the conditions seemed fairly steady before the accident happened, but the calculated results sometimes showed differences as large as 20 per cent from those obtained under better conditions.

IV. RESULTS AND DISCUSSION

It is to be borne in mind that the results presented in this paper are for particular specimens. Although the relative values for several types of construction may be considered fairly precise, it is quite probable that similar constructions in practice may differ to an appreciable extent from those tested here. Doubtless, quality of workmanship will be an important factor. To demonstrate this, two similar brick walls (Nos. 3 and 5) were built by different masons, and, as will be noted below, a difference of about 30 per cent in their insulating values was observed. These two specimens may possibly characterize the two extremes in workmanship. Therefore, in judging the absolute magnitude of the heat transfers, allowances must be made for such variations.

Results were obtained both with wood and cork conductimeters. An appreciable difference was found by these two conductimeters, but the results with the cork conductimeter were found to be much more consistent and reproducible.

These differences in behavior are not difficult to explain, and it seems desirable to discuss the question somewhat in detail, since points vital to the accuracy of this general method of measuring heat flow are involved.

It is quite evident that errors due to lateral heat flow in the system will be produced by a nonuniform or poor thermal contact between the conductimeter and the surface to which it is applied. If the contact consists of an air space of variable width, two distinct sources of error are present. The nonuniformity of contact causes a departure from normal heat flow within the conductimeter itself (the condition under which it was calibrated) and convection in the air space also causes heat flow in directions other than those perpendicular to the faces of the panels. At first it was thought that the contact between the wood conductimeter and the flat plaster surface would be sufficiently good, but due to the inconsistency of the results obtained, it was decided to build a more flexible conductimeter panel and provide means for pressing it firmly against the plaster surface at a large number of points. As mentioned above, the results obtained with the new conductimeter were reproducible with much greater precision than the old, and in addition were somewhat lower, as might be

expected since both of the sources of error mentioned above are more likely to cause too high a value for the calculated conductance of the panel. The fact that the thermal contact between the cork conductimeter and plaster surface was extremely good is indicated by the small temperature difference, averaging about 1° F., existing between the surfaces in contact. With the wood conductimeter the corresponding temperature differences were variable and much greater. It does not seem possible that the slightly better thermal contact which might be produced by cementing the surfaces together would have changed the results by any significant amount.

For the above reasons the data given in this paper are based entirely on the experiments made with the cork conductimeter. Calibrations of the conductimeter were made at frequent intervals.

TABLE 1.—*Calibration of cork composition conductimeter*

Date	Mean temperature	Calibration factor	Date	Mean temperature	Calibration factor
1924	° F.		1927	° F.	
Nov. 28, 29	103	12.5	Jan. 12, 13, 14	94	12.9
Dec. 1, 2, 3	77	12.7	Oct. 4, 10, 13	105	12.6
1925			1928		
Jan. 12, 13	97	12.1	Jan. 4, 5, 6	88	12.7
Feb. 17, 18, 19	97	12.4	Jan. 28	96	12.5
Mar. 17, 18	97	12.2	Jan. 30, Feb. 1, 2	84	12.6
Apr. 18, 19	97	12.7	Feb. 3, 4	141	12.2
May 9, 11	97	12.5	Mar. 23, 24	89	12.4
May 25, 26	97	12.4	July 5, 6, 9	105	12.9
			July 10, 11	138	12.8

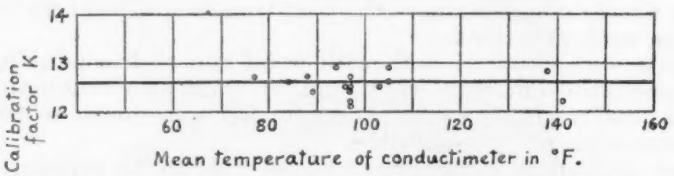

FIGURE 12.—*Calibration of cork composition conductimeters*

Table 1 gives the complete calibration data. In the second column is given the mean temperature of the conductimeter, and in the last column the calibration factor, which is the number of B. t. u. flowing through the conductimeter per hour, per square foot, per millivolt reading of the imbedded differential thermocouples. The fluctuations in the calibration factor are due probably to changes in the moisture content of the cork composition, a factor which is difficult to control. However, for all practical purposes an average value taken over a long period of time is sufficiently accurate for the purpose at hand. The conductivity of the cork composition increases with mean temperature, but this is practically compensated by a corresponding increase in the e. m. f. per degree of the copper-constantan couple used. The resultant effect is to yield a calibration factor which is practically independent of the mean temperature as shown in Figure 12.

Table 2 gives the complete data for all the walls tested. In the last column is given the resistance per unit area, which is the reciprocal of the conductance per unit area. The conductances and resistances do not include any surface effects. The mean temperature given in column 6 is the mean of the temperatures of the warm and cold surfaces of each wall.

All the curves in Figure 13 show, as would be expected, a decrease in resistance with increase in mean temperature. The slopes of the curves for the 8-inch solid walls are about what might be expected, judging from our rather scanty knowledge of the increase in conductivity with temperature of such materials as brick. The slopes of the curves for walls containing air spaces are naturally greater, on account of the very rapid increase in the heat transfer by radiation. In some cases, however, for example, walls No. 9, 11, 15, 16, and 17 the slopes are greater than can be accounted for by any known facts of radiation, conduction, or convection. A single case of this kind could easily be explained as fortuitous experimental error, but the effect appears to be systematic, and such an explanation for all cases is therefore improbable. It will be noted that the direction of the effect is such that it could be accounted for, qualitatively at least, by lateral heat flow in the wall specimen, resulting from exchange of heat between the edges of the specimen and the test room which was always maintained at nearly the same temperature during all tests on a single wall section. The measured resistances at mean temperatures below that of the test room would tend to be too high, and those at mean temperatures above that of the test room, too low.

TABLE 2.

Wall	Description	Temperature of warm air	Temperature of cold air	Temperature of plaster or warm surface of wall	Temperature of cold surface of wall	Mean temperature of wall	E. m. f. of conductimeter	Conductance of wall	Resistance of wall
		° *F.*	° *F.*	° *F.*	° *F.*	° *F.*	*Millivolts*	*B. t. u. per hr. per sq. per° F.*	*° F./ B. t. u. per hr. per sq. ft.*
No. 1	8-inch brick (Baltimore)	56.9	1.3	38.5	10.1	24.3	1.32	0.585	1.71
		105.6	42.7	83.7	52.0	67.8	1.61	.64	1.56
		92.5	28.1	70.5	37.6	54.1	1.63	.62	1.60
		79.6	15.5	58.7	26.8	42.8	1.57	.62	1.60
No. 2	8-inch brick (New England)	75.5	21.2	53.8	32.4	43.1	1.52	.90	1.11
		56.6	15.3	41.7	24.9	33.3	1.05	.79	1.26
		92.3	37.9	72.9	52.4	62.7	1.45	.89	1.12
		113.8	49.7	91.3	65.8	78.5	1.70	.84	1.19
		87.6	21.4	62.4	35.2	48.8	1.81	.84	1.19
		80.6	15.9	54.9	28.4	41.7	1.95	.93	1.08
		117.8	37.7	85.9	53.3	69.6	2.46	.95	1.05
		126.6	32.4	90.0	49.8	69.9	2.79	.87	1.14
No. 3	8-inch brick (Mississippi)	121.8	34.2	89.8	51.3	70.6	2.33	.76	1.31
		86.6	23.7	63.6	37.4	50.5	1.56	.75	1.33
No. 4	12-inch brick	82.9	21.9	64.5	33.8	49.1	1.22	.50	2.00
		128.5	42.4	98.5	54.6	76.6	2.12	.61	1.64
		80.2	17.2	61.4	29.2	45.3	1.26	.49	2.03
No. 5	8-inch brick	131.1	48.1	101.1	58.8	80.0	2.00	.595	1.68
		90.6	24.7	68.3	35.2	51.7	1.44	.55	1.82
No. 6	8-inch furred brick	110.5	34.1	90.0	43.9	67.0	1.49	.41	2.45
		68.0	5.0	52.9	15.1	34.0	1.07	.36	2.80
		65.5	−4.4	48.7	5.9	27.3	1.18	.35	2.88
		105.1	43.5	87.8	52.0	69.9	1.21	.425	2.35

TABLE 2.—Continued

Wall	Description	Temperature of warm air	Temperature of cold air	Temperature of plaster or warm surface of wall	Temperature of cold surface of wall	Mean temperature of wall	E. m. f. of conductimeter	Conductance of wall	Resistance of wall
								B. t. u. per hr. per sq. per° F.	*° F./ B. t. u. per hr. per sq. ft.*
		° *F.*	° *F.*	° *F.*	° *F.*	° *F.*	*Millivolts*		
No. 7	8-inch rolokbak	134.6	49.1	106.8	61.0	83.9	1.99	0.55	1.83
		86.9	27.4	69.3	36.4	52.9	1.21	.46	2.16
		86.5	31.3	69.7	38.8	54.2	1.19	.485	2.06
No. 8	8-inch all rolok	147.8	51.2	115.1	64.3	89.7	2.51	.62	1.61
		87.7	25.7	68.1	36.2	52.2	1.39	.55	1.82
		90.0	34.0	72.3	42.6	57.5	1.31	.555	1.80
No. 9	do	119.4	51.4	95.3	58.5	76.9	1.81	0.62	1.61
		82.6	33.1	68.0	39.9	54.0	1.05	.47	2.12
		81.2	30.7	66.1	38.9	52.5	1.07	.495	2.02
		121.0	55.1	97.5	61.3	79.4	1.81	.63	1.59
		125.1	58.7	101.7	65.4	83.6	1.85	.64	1.56
No. 10	8-inch hollow tile (end construction).	67.8	8.1	52.0	14.2	33.1	1.06	0.35	2.83
		84.0	22.3	67.1	27.9	47.5	1.19	.38	2.62
		113.6	46.1	94.9	52.8	73.8	1.38	.41	2.42
No. 11	8-inch hollow tile (side construction).	68.9	11.6	54.5	20.5	37.5	1.03	0.38	2.62
		92.5	31.8	73.8	38.7	56.2	1.25	.45	2.23
		91.2	32.2	73.6	38.5	56.0	1.20	.43	2.32
		109.4	40.6	87.8	48.4	68.1	1.49	.48	2.10
No. 12	8-inch hollow tile (double shell).	73.0	22.0	58.4	27.8	43.1	1.02	0.42	2.38
		92.6	44.2	77.9	49.0	63.4	1.06	.46	2.16
		122.9	63.4	104.6	69.6	87.1	1.41	.51	1.97
No. 13	8-inch hollow tile (two unit)	76.1	17.2	60.8	21.4	41.1	1.025	0.33	3.05
		95.9	32.0	77.6	36.7	57.1	1.22	.38	2.66
		122.9	47.3	100.9	52.7	76.8	1.50	.39	2.56
No. 14	8-inch cement block	99.0	32.9	70.3	38.1	54.2	1.96	0.77	1.30
		97.7	30.2	67.8	34.4	51.1	2.03	.765	1.31
		53.8	0.3	29.2	3.8	16.5	1.45	.72	1.39
		114.3	59.6	91.6	63.2	77.4	1.64	.73	1.38
No. 15	4-inch frame (furred)	104.7	66.9	95.7	72.6	84.1	0.66	0.36	2.79
		102.0	56.6	92.6	62.9	77.8	.745	.32	3.16
		94.0	49.0	84.8	54.7	69.8	.69	.29	3.48
		71.6	20.5	62.8	25.0	43.9	.69	.23	4.37
		108.1	58.8	97.8	66.5	82.2	.79	.32	3.13
		90.5	40.3	81.0	45.6	63.3	.76	.27	3.69
		96.2	52.7	88.3	63.1	75.7	.65	.33	3.07
		69.2	20.4	62.2	26.2	44.2	.63	.22	4.55
		112.3	47.1	100.2	62.2	81.2	.90	.30	3.36
		74.9	15.7	62.6	22.5	42.5	.68	.21	4.66
		128.2	92.0	119.7	94.0	106.9	.695	.34	2.94
		130.8	95.0	122.0	97.3	109.7	.69	.35	2.86
No. 16	4-inch frame	130.5	72.3	115.2	79.1	97.2	1.18	0.41	2.43
		80.5	35.0	71.5	41.2	56.3	0.68	.28	3.54
		93.3	53.9	83.3	59.0	71.1	0.705	.37	2.73
		77.2	31.7	67.0	36.9	52.0	.685	.29	3.49
No. 17	Air space	120.4	56.8	97.5	66.6	82.1	1.63	0.66	1.51
		73.9	30.6	60.3	37.3	48.8	.92	.505	1.98
		90.8	46.6	75.6	52.7	64.1	1.05	.58	1.73

In considering the lateral heat flow by conduction in a solid wall, only the width and thickness have to be considered as a first approximation, since the specimens are twice as tall as they are wide. If the mean temperature of the wall differs from that of the test room, the temperature distribution in the central region will be affected to some extent. For a 9-inch solid wall, however, it can be shown by

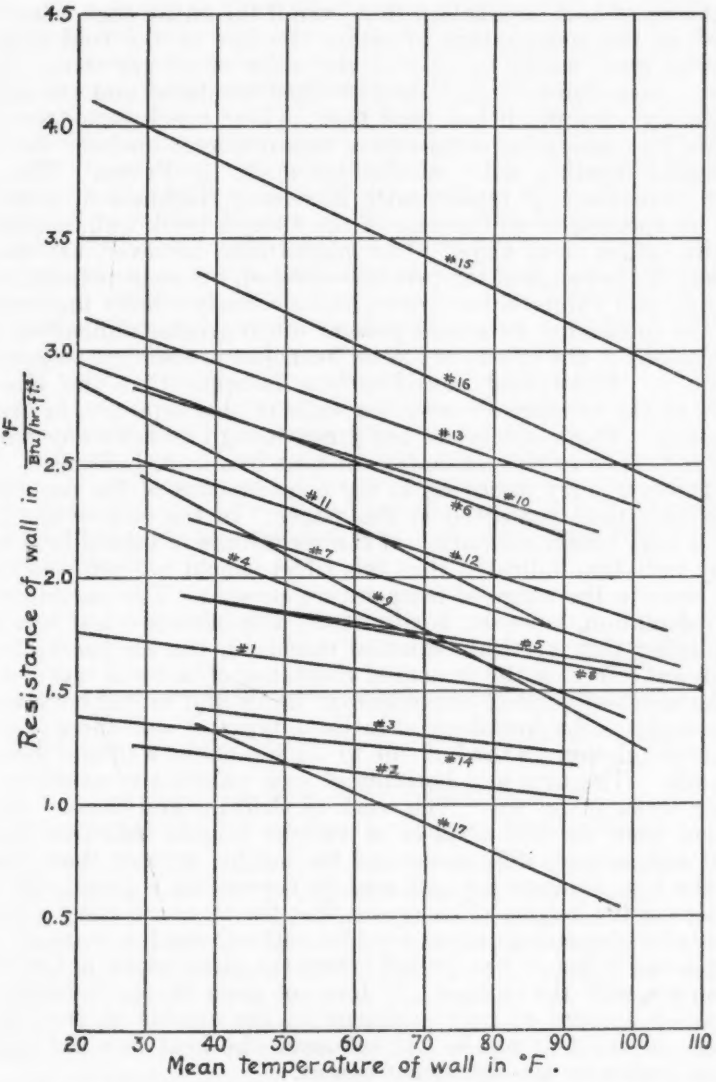

FIGURE 13.—*Resistance of walls for various mean temperatures*

No. 1, 8-inch brick (Baltimore).
No. 2, 8-inch brick (New England).
No. 3, 8-inch brick (Mississippi).
No. 4, 12-inch brick.
No. 5, 8-inch brick; furrowed horizontal joints; unfilled vertical longitudinal joints.
No. 6, 8-inch furred brick.
No. 7, 8-inch rolokbak.
No. 8, 8-inch all rolok.
No. 9, 8-inch all rolok.
No. 10, 8-inch hollow tile (end construction).
No. 11, 8-inch hollow tile (side construction).
No. 12, 8-inch hollow tile (double shell).
No. 13, 8-inch hollow tile (two unit).
No. 14, 8-inch Portland cement block.
No. 15, 4-inch frame (furred).
No. 16, 4-inch frame (without stucco and furring).
No. 17, air space.

the theory of heat conduction that even if the entire edge were maintained at the temperature of either the hot or the cold side, the resulting error would be only of the order of 10 per cent. In the present measurements the edges are well insulated and the error is necessarily very much less than this. These conclusions have been reached by considering temperature measurements made on the edges of panels, together with calculations made by Peirce.[6] The edge effect increases very rapidly with increasing thickness of panel and may be appreciable in the case of the 13-inch brick wall, accounting for the rather steep slope. The magnitudes, however, are not significant in the range of temperature covered, but extrapolation of the experimental values is hazardous and obviously wholly unnecessary.

Walls containing air spaces present much greater difficulties, since calculations of the effects of lateral heat flow are subject to great uncertainty. Theoretical considerations indicate that the observed slopes of the resistance curves for walls of this type are, in general, too steep. These effects are not great enough to have any particular significance in the estimation of heat loss from buildings. They are, however, very annoying in the consideration of the accuracy of the observations presented in this paper. In the case of the frame wall, a very rough estimation of the magnitude of lateral heat transfer by radiation indicated that this effect should not produce significant error in the range of temperature covered. The uncertainty in this calculation, however, is admitted. Experimental test was made by placing thin vertical radiation shields in the air space, but no significant effect on the measured resistance of the wall was noted.

The effect of vertical convection in frame and in end construction tile remains to be considered. In these types of wall there is a path for air circulation up the hot side to the top of the wall and down the cold side. The tops and bottoms of such panels are sealed, so that no air leaks in or out. The work of Griffiths and Davis [7] on convection from vertical surfaces of various heights indicates that for small temperature differences and for heights greater than about 2 feet the heat transfer per unit area by convection is practically independent of the height. This means that the air rising along a warmer surface (or descending along a colder surface) reaches a steady state after about 2 feet of rise (or fall) from the place where it first comes in contact with the surface. It does not seem likely, therefore, that the small amount of heat exchange to the outside at the top and bottom of the test panels will influence the heat flow through the central region to any significant extent.

Another possible source of error is present in the case of the frame walls tested, which would not tend to cause too steep a slope of the resistance curve, but would be in the same direction throughout the range of temperature covered. The test panel has a central vertical stud, which offers a path of considerably greater resistance to heat flow than the same area of air space. There is a possibility that the temperature distribution over the plaster surface would be sufficiently nonuniform to cause significant error in the conductimeter readings. To determine whether such an effect is appreciable, a flat copper plate, 1 foot square and one-sixteenth inch thick was cemented on the plaster surface immediately over the area covered by the conducti-

[6] Proc. Am. Acad. Arts and Sci., 45, p. 353; 1910.
[7] Special Report No. 9, Dept. Sci. Ind. Research, Great Britain.

meter. On account of the high thermal conductivity of copper, any lateral temperature gradients in the plaster surface would be greatly reduced. Observations made under these conditions showed no systematic change in the measured resistance of the panel.

The cause of the observed steepness in the resistance curves of certain walls still remains obscure, but it is probable that the effects are bound up in some way with the departure of the mean temperature of the wall specimen from the temperature of the test room. It is worthy of note that Rowley and his associates,[8] working with walls containing air spaces, observed these effects to a much greater degree. Other experimenters in this field have paid little or no attention to the variation of resistance with temperature. The existence of other sources of error might be mentioned, such as slow absorption or evaporation of moisture during test; conceivably producing a false, steady state, or peculiar effects of convection in the air spaces. It will be observed that all these hypothetical effects are intimately connected with the departure of the mean temperature of the wall from test-room temperature. Their magnitude and even their direction, however, is problematical. Extensive investigation with elaborate apparatus could no doubt clear up these discrepancies, but in view of the uncertain nature of the individual wall such refinements would appear to be superfluous.

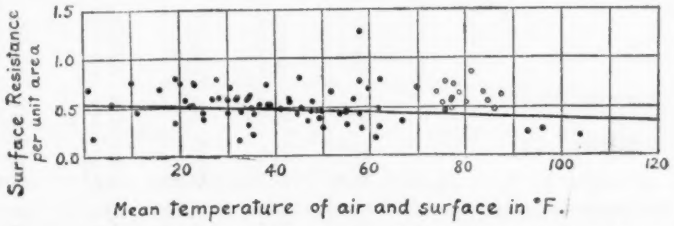

FIGURE 14.—*Surface resistances for different mean temperatures*

It may be concluded, however, that the magnitude of the discrepancies discussed above are not great enough to have any particular significance in the estimation of heat losses through building walls in the range of temperature they experience under ordinary conditions.

Little significant information was gained from the data on temperature distribution in the interior of the walls. The indications are, however, that the isothermal surfaces are practically plane over the central region, but due to the nonuniform nature of the walls, and the difficulty in precise location of the thermocouples, the observations have no great significance.

The data on surface resistance obtained in these experiments are shown in Table 3 and Figure 14. The precision of these data is limited, since the temperature differences between the air and the surfaces were rather small. In any case, however, the results apply only to the particular conditions existing in the apparatus. The abscissa in Figure 14 is the mean of the temperature of the surface and that of the air, the latter being measured by a couple about 3 inches from the surface. The ordinate is the resistance per unit area in °F for a heat flow of 1 B. t. u. per hour per square foot between the air and surface.

[8] J. Am. Soc. Heating and Ventilating Eng., **34**, 7; p. 529; July, 1918.

As already noted, it was necessary to create considerable air motion in order to maintain a uniform temperature distribution over the test panel, and the results apply for this air velocity (about 5 miles per hour) and not for natural convection. They represent, perhaps, a rough average between usual inside and outside conditions. If two such surface resistances be added to the resistance of a wall, the sum will represent the total resistance of a wall under average conditions as nearly as it is possible to define them.

TABLE 3

Wall	Description	Temperature of cold surface	Temperature of cold air	Δt	Heat flow	Surface resistance	Mean temperature of surface
		°F.	°F.	°F.	B. t. u. hr.$^{-1}$ ft.$^{-2}$		°F.
No. 1	8-inch brick (Baltimore)	10.1	1.3	8.8	16.6	0.53	5.7
		52.0	42.7	9.3	20.3	.46	47.4
		37.6	28.1	9.5	20.5	.46	32.8
		26.8	15.5	11.3	19.8	.57	21.2
No. 2	8-inch brick (New England)	32.4	21.2	11.2	19.1	.59	26.8
		24.9	15.3	9.6	13.2	.73	20.1
		52.4	37.9	14.5	18.3	.79	45.2
		65.8	49.7	16.1	21.4	.75	57.8
		35.2	21.4	13.8	22.8	.60	28.3
		28.4	15.9	12.5	24.6	.51	22.2
		53.3	37.7	15.6	31.0	.50	45.5
		49.8	32.4	17.4	35.2	.49	41.1
No. 3	8-inch brick (Mississippi)	51.3	34.2	17.1	29.4	.58	42.8
		37.4	23.7	13.7	19.6	.70	30.6
No. 4	12-inch brick	33.8	21.9	11.9	15.4	.77	27.8
		54.6	42.4	12.2	26.7	.46	48.5
		29.2	17.2	12.0	15.9	.75	23.2
No. 5	8-inch brick	58.8	48.1	10.7	25.2	.42	53.4
		35.2	24.7	10.5	18.1	.58	30.0
No. 6	8-inch furred brick	43.9	34.1	9.8	18.9	.52	39.0
		15.1	5.0	10.1	13.5	.75	10.0
		5.9	−4.4	10.3	14.9	.69	0.8
		52.0	43.5	8.5	15.2	.56	47.8
No. 7	8-inch rolokbak	61.0	49.1	11.9	25.1	.47	55.0
		36.4	27.4	9.0	15.2	.59	31.9
		38.8	31.3	7.5	15.0	.50	35.0
No. 8	8-inch all rolok	64.3	51.2	13.1	31.6	.41	57.8
		36.2	25.7	10.5	17.5	.60	32.0
		42.6	34.0	8.6	16.5	.52	38.3
No. 9	8-inch all rolok	58.5	51.4	7.1	22.8	.31	55.0
		39.9	33.1	6.8	13.2	.52	36.5
		38.9	30.7	8.2	13.5	.61	34.8
		61.3	55.1	6.2	22.8	.27	58.2
		65.4	58.7	6.7	23.3	.29	62.0
No. 10	8-inch hollow tile (end construction).	14.2	8.1	6.1	13.4	.46	11.2
		27.9	22.3	5.6	15.0	.37	25.1
		52.8	46.1	6.7	17.4	.38	49.4
No. 11	8-inch hollow tile (side construction).	20.5	11.6	8.9	13.0	.68	16.0
		38.7	31.8	6.9	15.2	.44	30.2
		38.5	32.2	6.3	15.1	.42	35.4
		48.4	40.6	7.8	18.8	.42	44.5
No. 12	8-inch hollow tile (double shell)	27.8	22.0	5.8	12.9	.45	24.9
		49.0	44.2	4.8	13.4	.36	46.6
		69.6	63.4	6.2	17.8	.35	66.5
No. 13	8-inch hollow tile (two unit)	21.4	17.2	4.2	12.9	.33	19.3
		36.7	32.0	4.7	15.4	.31	34.4
		52.7	47.3	5.4	18.9	.29	50.0

TABLE 3.—Continued

Wall	Description	Temperature of cold surface	Temperature of cold air	Δt	Heat flow	Surface resistance	Mean temperature of surface
		° F.	° F.	° F.	B. t. u. hr.$^{-1}$ ft.$^{-2}$		° F.
No. 14	8-inch cement block	38.1	32.9	5.2	24.7	0.21	35.5
		34.4	30.2	4.2	25.6	.16	32.3
		3.8	.3	3.5	18.3	.19	2.0
		63.2	59.6	3.6	20.6	.17	61.4
No. 15	4-inch frame (furred)	72.6	66.9	5.7	8.3	.69	69.8
		62.9	56.6	6.3	9.4	.67	59.8
		54.7	49.0	5.7	8.7	.65	51.8
		25.0	20.5	4.5	8.7	.52	22.8
		66.5	58.8	7.7	10.0	.77	62.6
		45.6	40.3	5.3	9.6	.55	43.0
		63.1	52.7	10.4	8.2	1.27	57.9
		26.2	20.4	5.8	7.9	.73	23.3
		62.2	47.1	5.1	11.4	.45	54.6
		22.5	15.7	6.8	8.6	.79	19.1
		94.0	92.0	2.0	8.8	.23	93.0
		97.3	95.0	2.3	8.7	.26	96.2
No. 16	4-inch frame	79.1	72.3	6.8	14.9	.46	75.7
		41.2	35.0	6.2	8.6	.72	38.1
		59.0	53.9	5.1	8.9	.57	56.4
		36.9	31.7	5.2	8.6	.60	34.3
No. 17	Air space	66.6	56.8	9.8	20.6	.48	61.7
		37.3	30.6	6.7	11.6	.58	34.0
		52.7	46.6	6.1	13.2	.46	49.6

V. TESTS ON SMALL PANELS BY HOT-PLATE METHOD

A series of tests was made on small panels, each of which is a component of frame wall construction. The apparatus used in these tests is different from that described above for the large walls. It consists of a flat electric heater built with an edge heater according to the usual designs of a hot plate for thermal conductivity apparatus outside total dimensions being 24 inches square. The panels tested [9] were 32 by 32 inches in total area, two specimens of each type being used in each test. Thermocouples were pasted on both surfaces of each panel, as well as on the surfaces of the hot plate. One specimen was placed on each side of the heater and the whole combination was clamped together. Considerable insulation was wrapped around the edge. Thermometers were hung in the air, about 4 inches from the surface of each panel. In each case the sheathing was placed against the hot plate.

The results of these tests are given in Table 4 and Figure 15. The data on surface resistance per unit area given in columns 10 and 11 is plotted with the previous data in Figure 14. It will be noted that the group of points in Figure 14 (those represented by circles) which give the surface resistances obtained by this second method, are higher than the average indicated by the previous points. This is explained by the difference in the air velocities along the surfaces in the two cases. In the latter experiments there were no forced convection, but merely that which would arise through a temperature difference between the surface and the air in the vicinity.

[9] J. Am. Soc. Heating and Ventilating, Eng., **26**, 7, p. 637; October, 1920.

TABLE 4.—*Observations made with hot plate 24 inches square*

Wall	Description	Temperature of hot surface	Temperature of cold surface	Temperature of adjacent air	Heat flow	Conductance of panel	Resistance of panel	Mean temperature of panel	Conductance of surface	Resistance of surface	Mean temperature of surface and air
		° F.	° F.	° F.	*B.t.u. hr.$^{-1}$ ft.$^{-2}$*	*B.t.u. hr.$^{-1}$ ft.$^{-2}$ deg.$^{-1}$ F.*					
No. 18..	¾-inch sheathing, paper.....	152.2	100.9	73.8	43.0	0.84	1.19	126.6	1.59	0.63	87.4
		128.4	92.9	74.2	29.2	.82	1.22	110.7	1.56	.64	83.6
		102.4	82.9	72.0	15.1	.78	1.29	92.7	1.39	.72	77.4
No. 19..	¾-inch sheathing, paper, shingles.	129.8	84.4	73.2	17.9	.395	2.53	107.1	1.60	.63	78.8
		101.6	78.8	72.3	8.7	.38	2.61	90.2	1.34	.75	75.6
No. 20..	¾-inch sheathing, paper, clapboards.	102.0	79.9	74.4	9.5	.43	2.32	91.0	1.73	.58	77.2
		157.3	93.2	75.9	31.7	.49	2.03	125.2	1.83	.55	84.6
No. 21..	¾-inch sheathing, paper, clapboards, paper, shingles.	135.5	84.3	76.6	14.3	.28	3.58	109.9	1.86	.54	80.4
		95.0	75.1	72.0	4.8	.24	4.18	85.1	1.55	.65	73.6
		144.9	87.8	74.6	15.7	.275	3.64	116.3	1.19	.84	81.2
		142.4	81.2	72.5	15.5	.25	3.96	111.8	1.78	.56	76.8
		99.8	76.9	73.7	5.1	.22	4.49	88.3	1.59	.63	75.3
No. 22..	¾-inch sheathing, paper, ¾-inch furring air space, metal lath, stucco.	89.1	78.5	76.0	5.1	.48	2.07	83.8	2.04	.49	77.2
		156.1	93.9	78.0	33.3	.535	1.87	125.0	2.09	.48	86.0

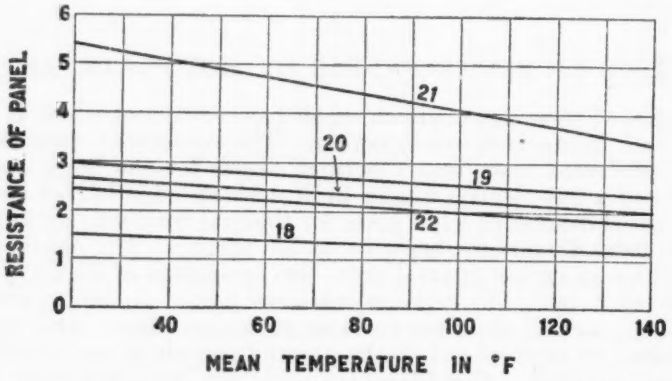

FIGURE 15.—*Resistances of panels tested with 24 by 24 inch hot plate*

VI. CALCULATION OF THE CONDUCTANCE, RESISTANCE, AND TRANSMITTANCE OF WALLS AND THEIR COMPONENT PARTS

In order to make data on the heat transmission through walls of basic value in the design and study of building structures, it is not only necessary to know what the values are for any particular construction, but it is essential to be able to calculate beforehand what the values might be for any desired combination of materials. To conduct tests on all possible combinations is entirely impracticable. It is possible, however, to utilize the ordinary simple laws of heat flow and, with a knowledge of the values for a relatively few basic constituents, to compute the conductance, resistance, and transmit-

tance per unit area of any combination of these components with reasonable accuracy. In this section an analysis is made of the data on the complete walls, and values are obtained for the various components as well as for a number of walls which have not been tested.

It should be noted that certain components that are cited in Table 5 are somewhat hypothetical. For example, in considering the resistance of the furring air space, what is meant is the resistance of that given width of space set off by furring strips, where the two surfaces are inclosed, either by paper, sheathing, or any other solid material, but does not include spaces open on one side.

TABLE 5.—*Values for walls and component parts at a mean temperature of 50° F.*

[Values of resistance R, conductance C, and transmittance T based on a value of surface resistance equal to 1.0. The following are values taken from the curves of Figures 13 and 15]

Item	Description	R	C	$T=\frac{1}{1+R}$
1	8-inch brick, ¾-inch plaster (average of walls Nos. 1, 2, and 3)	1.37	0.73	0.42
2	8-inch brick, ⅞-inch furring (inside), ¾-inch plaster (wall No. 6)	2.61	.38	.28
3	8-inch hollow tile, end construction, plaster, stucco (wall No. 10)	2.63	.38	.28
4	8-inch hollow tile, side construction, plaster, stucco (wall No. 11)	2.39	.42	.295
5	8-inch hollow tile, end construction, plaster only (wall No. 12)	2.31	.43	.30
6	8-inch hollow tile, end construction, plaster, stucco (wall No. 13)	2.84	.35	.26
7	8-inch hollow cement block, ¾-inch plaster (wall No. 14)	1.30	.77	.435
8	Frame: wood lath and plaster, 2 by 4 studs, sheathing, paper, ⅞-inch furring (outside), metal lath and stucco (wall No. 15)	4.11	.24	.20
9	Same as 8, less furring (outside), metal lath and stucco (wall No. 16)	3.43	.29	.23
10	8-inch rolokbak, ¾-inch plaster (wall No. 7)	2.14	.47	.32
11	8-inch all-rolok, ¾-inch plaster (average of walls Nos. 8 and 9)	1.98	.505	.34
12	¾-inch sheathing, paper (wall No. 18)	1.40	.71	.42
13	¾-inch sheathing, paper, shingles (wall No. 19)	2.81	.36	.26
14	¾-inch sheathing, paper, clapboards (wall No. 20)	2.50	.40	.29
15	¾-inch sheathing, paper, clapboards, paper, shingles (wall No. 21)	4.92	.20	.17
16	¾-inch sheathing, paper, ¾-inch furring, metal lath and stucco (wall No. 22)	2.26	.44	.31

In Table 5 the values have been taken from the curves of Figure 13, and correspond to a mean temperature of 50° F. C is the conductance in B. t. u. per hour per square foot per ° F. temperature difference between the surfaces of the wall. R is the resistance, and is numerically equal to $1/C$.

In all these calculations the total resistance of the two surfaces of a wall is taken as equal to 1° F. per unit heat flow (1 B. t. u. per hour per square foot). This is believed to be a reasonably good average value for ordinary temperatures and air velocities. The resistance of a wall figured from air to air will then be 1 plus the resistance from surface to surface. T is the transmittance and is defined numerically as being equal to $1/(1+R)$.

In computing the values given in Table 6, the following additional values have been used, where k is the thermal conductivity in B. t. u. per hour per square foot per ° F. per inch.

	k
Plaster	2.3
Cement mixture	3.8
White pine	.8

In calculating the value for wood lath and plaster, the dimensions for the lath were taken as 1⅜ by 5/16 inch, and spaced apart one-fourth inch. The value for wood lath and plaster given in the table was calcula-

ted on the basis that plaster was keyed into the spacings between the lath to a depth of five-sixteenths inch, and in addition for a thickness of three-fourths inch from the surface of the lath.

TABLE 6.—*Derived data for use in calculations*

[The following values are based on estimated values of the thermal conductivity of each material concerned]

Item	Description	*R*	*C*
17	¾-inch plaster (with or without metal lath)	0.33	3.03
18	¾-inch stucco	.20	5.00
19	Wood lath, ¾-inch plaster	.63	1.59

[The following values are derived from the data on walls nos. 1 and 6, fig. 13, taking into account the mean temperature of the furring air space for different mean temperatures of the entire wall No. 6.]

Item	Description	*R*	*C*
20	⅞-inch furring air space, 55° to 60° F. mean temperature; to be referred to as "inside furring"	0.96	1.04
21	⅞-inch furring air space, 35° to 40° F. mean temperature; to be referred to as "outside furring"	1.10	0.91

[The following values for components and complete walls are based on all of above values, derived as indicated]

Item	Description	*R*	*C*	*T*
22	8-inch brick (1—17)	1.04	0.96	0.49
23	4-inch brick	.52	1.92	.66
24	12-inch brick	1.56	.64	.39
25	4-inch brick, ¾ inch plaster (23+17)	.85	1.18	.54
26	12-inch brick, ¾ inch plaster (24+17)	1.89	.53	.35
27	4-inch brick, inside furring, metal lath and plaster (23+20+17)	1.81	.55	.36
28	4-inch brick, inside furring, wood lath and plaster (23+20+19)	2.11	.47	.32
29	8-inch brick, inside furring, wood lath and plaster	2.63	.38	.28
30	12-inch brick, inside furring, wood lath and plaster	3.15	.32	.24
31	8-inch hollow tile (average of items 3, 4, 5, and 6, in each case subtracting the plaster and stucco)	2.06	.485	.33
32	4-inch hollow tile	1.03	.97	.49
33	4-inch hollow tile, ¾ inch plaster	1.36	.735	.42
34	8-inch hollow tile, ¾ inch plaster	2.39	.42	.295
35	4-inch hollow tile, stucco, inside furring, metal lath and plaster	2.52	.40	.28
36	4-inch hollow tile, stucco, inside furring, wood lath and plaster	2.82	.355	.26
37	8-inch hollow tile, stucco, inside furring, wood lath and plaster	3.85	.26	.21
38	4-inch hollow tile, stucco, plaster	1.56	.64	.39
39	8-inch hollow tile, stucco, plaster	2.59	.39	.28
40	4-inch hollow tile, 4-inch brick veneering, plaster	1.88	.53	.35
41	8-inch hollow tile, 4-inch brick veneering, plaster	2.91	.34	.26
42	2 by 4 studs (8—19—12—21—18)	.78	1.28	
43	2 by 4 studs (9—19—12)	1.40	.71	
44	2 by 4 studs (average of 42 and 43)	1.09	.92	
45	Shingles (13—12)	1.41	.71	
46	Clapboards (14—12)	1.10	.91	
47	Stud partition, wood lath and plaster on both sides	2.35	.425	.30
48	Wood lath and plaster, studs, sheathing, paper, shingles (19+44+13)	4.53	.22	.18
49	Wood lath and plaster, studs, sheathing, paper, clapboards (19+44+14)	4.22	.24	.19
50	4-inch brick veneer, outside furring, sheathing, paper, studs, wood lath and plaster	4.74	.21	.175
51	8-inch rolokbak, no coatings	1.81	.55	.36
52	8-inch all-rolok, no coatings	1.65	.61	.38
53	8-inch rolokbak, inside furring, wood lath and plaster	3.40	.29	.23
54	8-inch all-rolok, inside furring, wood lath and plaster	3.24	.31	.24
55	8-inch rolokbak, sheathing, paper, studs, wood lath and plaster	4.93	.20	.17
56	8-inch all-rolok, sheathing, paper, studs, wood lath and plaster	4.77	.21	.17
57	8-inch rolokbak, 4-inch hollow tile, plaster	3.17	.32	.24
58	8-inch all-rolok, 4-inch hollow tile, plaster	3.01	.33	.25
59	8-inch hollow cement blocks, no coatings	.97	1.03	.51
60	8-inch hollow cement blocks, inside furring, wood lath and plaster	2.56	.39	.28

VII. REVIEW AND COMPARISON OF DATA BY PREVIOUS EXPERIMENTERS

Many of the data of previous experimenters have been omitted here because they relate to structures much different from those examined in this paper. In the work of Bugge,[10] the values obtained on various structures are compared with one type selected as a standard; and since no absolute values for conductance are given, the data have not been considered here.

In the following, comparisons are made by adding the resistances of each component of the wall structure as described by the particular experiments, using the values of Tables 5 and 6 above. The total resistance thus obtained is compared with the total resistance (from surface to surface) computed directly from the data in each individual paper. In computing these resistances, wherever necessary and possible, the values of the surface resistances have been taken directly or calculated from data given in that particular paper. If no data are given in the papers the value for the resistance of the two external surfaces has been taken equal to 1.0.

Data by L. M. Arkley (Bulletin No. 1, 1919, School of Engineering Research, University of Toronto, pp. 115–129)

TESTS MADE IN 1912

Test No.	Description	R	
		Calculated	Arkley
1	8-inch hollow concrete block wall, not plastered; air spaces empty	0.97	0.59
4	8-inch hollow concrete block wall, air spaces empty, plaster on both sides	1.63	.97
7	8-inch hollow concrete block wall, air spaces empty; plaster on both sides; 1 layer of tarred building paper on high temperature side of wall	1.63	2.88
8	8-inch hollow concrete block wall, air spaces empty; plaster on both sides; 1 layer of asphalt paper on high temperature side of wall	1.63	2.80
9	9-inch brick wall, without plaster	1.17	1.55
10	----do	1.17	1.52
11	7¾-inch hollow tile; air spaces empty; no plaster	2.00	1.40

TESTS MADE IN 1913

1	12-inch tile wall, laid with hollow spaces horizontal	3.09	2.39
2	Same as of test No. 1, but with 1 layer of paper on high temperature side of wall	3.09	3.76
3	Same as of test No. 1, with 1 coat of dehydratine painted on high temperature side of wall	3.09	3.85
4	12-inch tile wall, laid with hollow spaces horizontal, plaster on both sides, each ⅝-inch thick	3.75	4.59
5	12-inch tile wall, laid with hollow spaces vertical and directly over each other	3.09	2.10
6	Same as of test No. 5, with 1 coat of dehydratine on high temperature side	3.09	3.00
7	Same as of test No. 5, plaster on both sides, each ⅝ inch thick	3.75	3.39

It appears that in some of the tests by Arkley, infiltration of air through the wall was appreciable, and the application of a layer of paper, or a coat of dehydratine, which in themselves have but slight thermal resistance, increased the resistance of the wall. In those cases where infiltration of air was negligible, Arkley's results are in fair agreement with those of this paper.

[10] Results of Test Houses Erected by the Norwegian Technical University; published by F. Bruns Bokhandels Forlag, Trondhjem, 1924.

Data by Willard and Lichty (University of Illinois, Bulletin No. 102, Vol. XV, No. 12; November 19, 1917)

Description	R	
	Calculated	W. and L.
8-inch brick wall	1.04	2.00
2-inch hollow tile, ½-inch plaster on each side	.96	1.00
4-inch hollow tile, ½-inch plaster on each side	1.47	1.67
6-inch hollow tile, ½-inch plaster on each side	1.99	2.13

Data by Kreuger and Erikson (Ingeniörs Vetenskaps Akademien, Handlingar Nr. 36; published by A. B. Gunnar Tissels Tekniska Förlag, Stockholm, 1924)

Type	Description	R	
		Calculated	K. and E.
Average of I-1 and I-3	18-inch brick, plaster on each side	2.78	3.84
Average of I-2 and I-4	12-inch brick, plaster on each side	2.00	2.64
I-16	Hollow brick construction, consisting of plaster, 2½-inch brick, 7½-inch air space, 2½-inch brick, and plaster.	2.02	2.79
I-24	12-inch hollow tile, plaster on each side	3.53	2.74
I-29	1-inch wood, 1-inch air space, 10-inch brick, plaster	3.25	4.32
K-1a	¾-inch wood, paper, 2 by 5 inch studs, paper, ¾-inch wood.	2.86	2.54

Data by Rowley, Morris, and Algren (Jour. A. S. H. V. E., 34, 1928; pp. 517–541)

[The following values not given in Table V, are based on tests made at the Bureau of Standards]

	R
½-inch gypsum board	0.38
¾-inch sheathing	.75
⅜-inch wood lath and ⅜-inch plaster	.63
Lap siding (same as clapboards)	1.10

Wall No.	Description	R	
		Calculated	R., M., and A.
7	½-inch gypsum board, studding, ¾-inch fir sheathing, paper and lap siding	3.32	3.51
7a	⅜-wood lath and ⅜-inch plaster, studding, ¾-inch fir sheathing, paper and lap siding	3.57	3.57
8	⅜-inch wood lath and ⅜-inch plaster, studding, ¾-inch fir sheathing, paper and lap siding	3.57	3.43
10	⅜-inch wood lath and ⅜-inch plaster, studding, insulating board B (Table 4 of R. M. and A.), paper and lap siding	4.49	4.23
11	½-inch insulating board B, ⅜-inch plaster, studding, ½-inch insulating board B, paper and lap siding	5.70	5.61
20	⅜-inch lath and ⅜-inch plaster, studding, ¾-inch fir sheathing, and lap siding (no paper)	3.57	3.58
21	8-inch 3-cell tile, 1-inch furring strips, insulating board B, ⅜-inch plaster, stucco on tile	5.06	4.82
22	8-inch 3-cell tile, plaster, stucco	2.43	2.20
23	½-inch insulating board G (Table 4 of R. M. and A.), studding, ½-inch insulating board G	3.84	3.53
24	8-inch 3-cell tile, 1-inch furring strips, ⅜-inch lath and ⅜-inch plaster, stucco on tile	3.85	3.56
25	½-inch insulation B, studding, ½-inch insulation B	4.19	4.09
26	½-inch insulation G, ⅜-inch plaster, studding, ½-inch insulation G, paper and lap siding	5.11	4.67
31	7/10-inch insulation B, ⅜-inch plaster, studding, 7/10-inch insulation B, siding	6.78	5.78

Data by E. Griffiths (Special Report No. 7, Building Research Board, Great Britain, Dept. of Sci. and Industrial Research; published in 1923)

No.	Description	R	
		Calculated	Griffiths
1	9-inch brick, cement mortar	1.17	1.42
2	8½-inch brick, lime mortar	1.11	1.73
8	6-inch hollow terra-cotta bricks, horizontal	1.55	1.25
	6-inch hollow terra-cotta bricks, vertical	1.55	1.22
9	6-inch hollow terra-cotta bricks, ½-inch plaster	1.77	1.24
11	Frame construction; ¾-inch clap boards, 1-inch rough boarding; 2 by 4-inch studs; wood, lath, and plaster	4.22	2.50

Some of the walls tested by Rowley, Morris, and Algren include insulation installed in a special manner, and it is useful to know the effect of these particular installations. The following values are based entirely on the data given by these experimenters. Under A is given a description of the insulation; under B, the method of application. In the column headed C is indicated the method of calculation, as for example resistance of wall No. 12 minus resistance of wall No. 7a; and under the column headed D is given the increase in resistance due to the addition of the insulating material installed in the particular manner.

	C	D
1 A. Quilted wood fiber between two layers of kraft paper; thickness=0.504 inch	No. 12—No. 7a	4.10
1 B. Flanged midway in air space between studding	No. 12—No. 8	
2 A. 40 sheets of newspaper, covered on each side with double waterproofed kraft paper	No. 14—No. 7a	2.79
2 B. Flanged midway in air space between studding	No. 14—No. 8	
3 A. Animal hair, lined on one side with tar paper, and on other side with heavy kraft paper; thickness =0.269 inch	No. 15—No. 7a	3.03
3 B. Flanged midway in air space between studding	No. 15—No. 8	
4 A. Quilted wood fiber between two layers of kraft paper; thickness=0.550 inch	No. 16—No. 7a	2.51
4 B. Nailed on studding under sheathing	No. 16—No. 8	
5 A. Porous gypsum material poured in place	No. 17—No. 7a	3.87
5 B. 3½ inches thick, poured between studding	No. 17—No. 8	
6 A. Semirigid board; thickness=0.567 inch	No. 19—No. 7a	1.79
6 B. Back against sheathing	No. 19—No. 8	
7 A. Paper felt treated on the surfaces with creosote for waterproofing; thickness=0.119 inch	No. 28—No. 7a	2.26
7 B. Two thicknesses of insulation spaced between studs to divide air space into three equal parts	No. 28—No. 8	
8 A. Same as 7 A	No. 29—No. 7a	1.79
8 B. One thickness of insulation nailed to each side of studs, bowed in at center 1¼ inch	No. 29—No. 8	

VIII. SUMMARY AND GENERAL CONCLUSIONS

A method is described for measuring the thermal resistance of building wall sections under laboratory conditions. In this method all effects of air infiltration which may take place under actual weather conditions are eliminated. Results are given for a number of typical walls, and tables are included showing the thermal resistances of all ordinary wall components, so that the resistance of any combination of these components can be calculated.

The following general conclusions may be drawn from the results of the tests described. These conclusions are, of course, limited to the test conditions.

1. In general, the presence of air spaces or pockets increases the insulating value of walls built of heavy clay products.

2. Furring materially increases the insulating value of ordinary types of walls.

3. The differences in insulating value between the various types of hollow tile walls tested are unimportant.

4. Judging by tests on two kinds of brick, representing approximately the two extremes in common brick manufacture, the kind of brick used in a brick wall is of little importance from the insulation standpoint alone.

5. The type of workmanship in a masonry wall may make a considerable difference in the insulating value, depending chiefly on the degree of filling of the mortar joints. Solidly filled vertical joints are not so effective from the insulation standpoint as partially filled joints.

6. The insulating value of all walls tested increases with decreasing temperature, the increase, in general, being more rapid with hollow walls than with solid walls.

It is pointed out that investigations carried out elsewhere indicate that air infiltration through finished walls plays a minor rôle in heat loss from buildings. The possibilities of heat loss by partial air penetration into hollow walls are discussed at some length, and it may be inferred that there is always a possibility that an individual wall of this type may be subject to air penetration effects of appreciable magnitude.

In conclusion, it might, perhaps, be emphasized that in an actual building, heat loss through windows, doors, and roof tend to level out the effect of differences in the walls themselves to a very considerable extent. It may, therefore, be said that although there are considerable differences in the insulating values of the various types of walls tested, the magnitude of these differences is not sufficient to make them a very important factor in the choice of building wall types, except, perhaps, in the case of relatively thin solid masonry without air spaces, where discomfort may be caused or moisture condensation produced by abnormally cold interior wall surfaces. As an illustration from another angle of the observed differences in uninsulated wall types, walls showing the lower insulating values could, by the addition of a half inch of good insulating material, be endowed with a thermal resistance approximately as great as those showing the higher insulating values in the tests described. The difference between the poorest and best wall from the viewpoint of thermal insulation (representing the extremes in ordinary uninsulated construction), is equivalent to approximately three-fourths inch of good insulating material.

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